

BEST AVAILABLE COPY

PCT

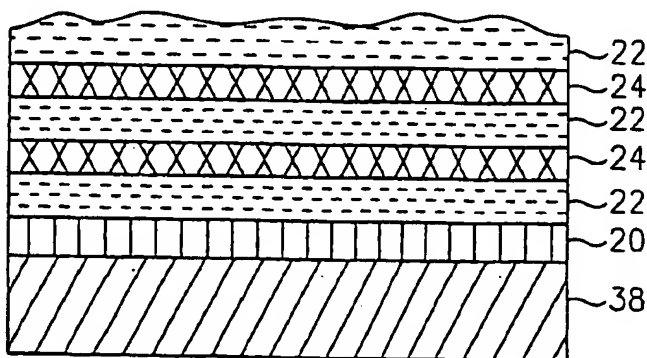
WORLD INTELLECTUAL PROPERTY ORGANIZATION
International Bureau



INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(51) International Patent Classification 7: H01L 51/20, H05B 33/04		A1	(11) International Publication Number: WO 00/26973
		(43) International Publication Date: 11 May 2000 (11.05.00)	
(21) International Application Number: PCT/US99/25843		(81) Designated States: AE, AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, CA, CR, CN, CU, CZ, DE, DK, DM, EE, ES, FI, GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MA, MD, MG, MK, MN, MW, MX, NO, NZ, PL, PT, RO, RU, SD, SE, SG, SI, SK, SL, TJ, TM, TR, TT, TZ, UA, UG, US, UZ, VN, YU, ZA, ZW, ARIPO patent (GH, GM, KE, LS, MW, SD, SL, SZ, TZ, UG, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, GW, ML, MR, NE, SN, TD, TG).	
(22) International Filing Date: 2 November 1999 (02.11.99)			
(30) Priority Data: 60/106,871 2 November 1998 (02.11.98) US 09/419,870 18 October 1999 (18.10.99) US			
(71) Applicant (for all designated States except US): DELTA V TECHNOLOGIES, INC. [US/US]; 7775 N. Casa Grande Highway, Tucson, AZ 85743 (US).			
(72) Inventor; and (75) Inventor/Applicant (for US only): BRIGHT, Clark, I. [US/US]; 7850 N. Silverbell, No. 114-107, Tucson, AZ 85743 (US).		Published With international search report With amended claims.	
(74) Agent: AUCIELLO, Lucinda, G.; Christie, Parker & Hale, LLP, P.O. Box 7068, Pasadena, CA 91109-7068 (US).			

(54) Title: TRANSPARENT CONDUCTIVE OXIDES FOR PLASTIC FLAT PANEL DISPLAYS



(57) Abstract

The present invention employs lightweight, flexible, plastic substrates for constructing flat panel displays, packaging materials and electro luminescence lamps. The display medium is protected from oxygen and moisture in order to avoid degradation. In the present invention, at least one layer with barrier and electrode characteristics is deposited over the substrate that has both a low enough resistivity to function as an electrode for the display and low oxygen and moisture permeability. For lower permeability and/or higher conductivity, multiple alternating layers of barrier materials and conductive materials are applied. The barrier material includes a thin metallic film, an organic polymer, a thin transparent dielectric, and a thin transparent conductive oxide. The conductive material includes a thin transparent conductive oxide, a thin transparent metallic film, and/or a metal nitride. Preferably there is a Polymer Multi Layer (PML) processed base coat deposited over the substrate. The base coat produces substrate smoothing, and more importantly, in combination with another layer, the base coat has vapor barrier properties. In the preferred embodiment, a PML processed top coat barrier layer is deposited before the coating contacts a surface, such as a roller. The PML processed top coat excludes moisture and atmospheric gases that chemically degrade the device performance.

FOR THE PURPOSES OF INFORMATION ONLY

Codes used to identify States party to the PCT on the front pages of pamphlets publishing international applications under the PCT.

AL	Albania	ES	Spain	LS	Lesotho	SI	Slovenia
AM	Armenia	FI	Finland	LT	Lithuania	SK	Slovakia
AT	Austria	FR	France	LU	Luxembourg	SN	Senegal
AU	Australia	GA	Gabon	LV	Latvia	SZ	Swaziland
AZ	Azerbaijan	GB	United Kingdom	MC	Monaco	TD	Chad
BA	Bosnia and Herzegovina	GE	Georgia	MD	Republic of Moldova	TG	Togo
BD	Barbados	GH	Ghana	MG	Madagascar	TJ	Tajikistan
BE	Belgium	GN	Guinea	ME	The former Yugoslav Republic of Macedonia	TM	Turkmenistan
BF	Burkina Faso	GR	Greece	ML	Mali	TR	Turkey
BG	Bulgaria	HU	Hungary	MN	Mongolia	TT	Trinidad and Tobago
BJ	Benin	IE	Ireland	MR	Mauritania	UA	Ukraine
BR	Brazil	IL	Israel	MT	Malawi	UG	Uganda
BY	Belarus	IS	Iceland	MX	Mexico	US	United States of America
CA	Canada	IT	Italy	NE	Niger	UZ	Uzbekistan
CF	Central African Republic	JP	Japan	NL	Netherlands	VN	Viet Nam
CG	Congo	KE	Kenya	NO	Norway	YU	Yugoslavia
CH	Switzerland	KG	Kyrgyzstan	NZ	New Zealand	ZW	Zimbabwe
CI	Côte d'Ivoire	KP	Democratic People's Republic of Korea	PL	Poland		
CM	Cameroon	KR	Republic of Korea	PT	Portugal		
CN	China	KZ	Kazakhstan	RO	Romania		
CU	Cuba	LC	Saint Lucia	RU	Russian Federation		
CZ	Czech Republic	LJ	Liechtenstein	SD	Sudan		
DE	Germany	LK	Sri Lanka	SE	Sweden		
DK	Denmark	LR	Liberia	SG	Singapore		
EE	Estonia						

1 TRANSPARENT CONDUCTIVE OXIDES FOR PLASTIC FLAT PANEL DISPLAYS

FIELD OF THE INVENTION

5 This invention relates to composite substrates for flat panel displays (FPD), packaging materials and light sources (electro luminescence lamps) comprising a plastic substrate having thin film barrier and conductive layers, in particular, multiple thin alternating layers of metallic film, transparent conductive oxide (TCO), metal nitride, and organic polymers deposited over the plastic substrate.

10 BACKGROUND OF THE INVENTION

The use of portable electronic devices incorporating flat panel displays is prevalent and increasing rapidly. Because of the portable nature of these devices, it is desired to minimize both the size and weight and maximize durability. The display portion of the device is generally larger and denser as compared to the rest of the device, and is manufactured on glass substrates. Accordingly, a smaller, lighter and more durable portable electronic device is most effectively achieved with a smaller, lighter and shatterproof electronic device display.

Despite being lightweight, plastic has not been considered a viable substrate material to be used for the manufacture of flat panel displays for multiple reasons. Most importantly, flat panel displays with plastic substrates tend to fail prematurely due to degradation of the display medium and some metallic electrodes. In particular, the display medium and some metallic electrodes become degraded when atmospheric oxygen and water permeate the substrate and chemically degrade the active portion of the display matrix, which is generally comprised of liquid crystals and/or light emitting devices. Second, common optical quality plastic substrates, e.g. polyethylene terephthalate (PET), have limited thermal properties. In particular, there is a limited temperature range that allows useful optical quality (e.g. clarity, transparency, uniform index of refraction) to be maintained, while maintaining the requisite mechanical strength and properties of the substrate.

SUMMARY OF THE INVENTION

30 The present invention is directed to the fabrication of flat panel displays on lightweight, flexible, plastic substrates. Because plastic substrates for FPDs are flexible, smaller and lighter than glass substrates, the electronic device with the plastic FPD is more portable, space-efficient and lightweight. In addition, electroluminescent and organic light emitting devices fabricated on flexible polymeric substrates in a coating process have lower manufacturing costs than those with glass substrates, and improved ruggedness.

35 A display medium of the flat panel display is sandwiched between two electrode layers. At least one of the electrodes is transparent for viewing of the display. The display medium is protected from oxidative degradation. In the present invention, at least one layer, having both

1 barrier characteristics and the ability to function as an electrode, is deposited over the substrate.
In particular, the layer has both low oxygen and moisture permeability, and a low enough
resistivity to function as an electrode for the display. For lower permeability and/or higher
conductivity, multiple alternating layers of barrier materials and conductive materials are
5 applied. In an alternative embodiment, the conductive layers are in direct contact. The barrier
material includes at least one of an organic polymer, a transparent dielectric, a transparent metal
nitride and/or a transparent conductive oxide. The conductive material includes at least one of
a thin transparent conductive oxide, a thin transparent metallic film and/or a metal nitride.

10 Using a smoothing base coat layer over the plastic substrate imparts good optical quality
throughout the substrate layers and provides a pristine surface for nucleation of the deposited
conductive layer, e.g. TCO. The pristine surface smooths over any surface roughness of the
plastic substrate, thereby adding to the FPD lifetime and optical quality. Additionally, a
hardcoat layer is applied over the substrate in lieu of or in addition to the smoothing basecoat
layer. The hardcoat layer provides increased barrier ability.

15 While the smoothing layer is applied by one of many well known non-vacuum liquid
coating processes, e.g. preferably by Gravure, the base coat is fabricated through a polymer
multilayer (PML) coating process. Related desirable coating processes are disclosed in U.S.
Patents 5,547,508, 5,395,644, 5,260,095, U.S. Patent Application Number 08/939,594, filed
September 29, 1997, entitled "*Plasma enhanced chemical deposition with low vapor pressure*
20 *compounds*" herein incorporated by reference, *Thin Film Processes II*, chapters II-2, 4, 5, and
IV-1, edited by John L. Vossen and Wermer Kern, Academic Press, 1991, ISBN 0-12-728251-
3, *Deposition Technologies for Films and Coatings, Developments and Applications*, Rointan
F. Bunshah et al, Noyes Publications, 1982, ISBN 0-8155-0906-5. Plasma PML processes
(PML and liquid PML) are called liquid multilayer (LML) processes. The PML process for
25 vacuum evaporation is used to deposit organic monomers over the plastic substrate. The
organic monomer is then polymerized in-situ by electron beam or UV radiation. The PML
process is compatible with physical vapor deposition processes for layers such as TCO layers.
Both processes are carried out in combined sequences within a properly designed single vacuum
chamber, however, multiple vacuum chambers are preferably used. The PML deposited organic
30 polymer layer is used to produce substrate surface smoothing and improve barrier coatings in
the multilayer structure. The benefit of a smooth substrate surface is that there is a clean surface
for adhesion, nucleation, and growth of a deposited conductive layer, e.g. a TCO. Additionally,
a PML deposited organic polymer layer provides protection of an underlying barrier layer in
order to minimize holes or other defects in the layer so that there is low permeability.

35 A single layer coating with metal oxide layers, such as thin film dielectric coatings
(alumina or silica or other certain metal oxides), or thick metallic film layers having optical
densities greater than 2.0 on plastic flat panel displays does not render low enough permeability
for the processing and manufacture of these displays with acceptable lifetimes. Even where

1 multiple layers of dielectrics, metals or the combination thereof are used, the improvement in
performance is minimal. In order to provide barrier properties sufficient for optical quality
plastic flat panel displays, a transparent dielectric barrier, such as SiO_{2-x} or $\text{Al}_2\text{O}_{3-y}$, is deposited
over a plastic substrate. When dielectric layers are combined with PML deposited organic
5 polymer layers, outstanding barrier properties are achieved on flexible plastic substrates.
Alternatively to the dielectric layer, a barrier coating of ITO (called "indium tin oxide", which
is actually "Tin doped indium oxide," a mixture of indium oxide and tin oxide) or another TCO
barrier is deposited over the substrate. In yet another alternative embodiment, both TCO barrier
layers and PML processed organic polymer layers are deposited over the plastic substrate.
10 Moreover, in yet another alternative, both TCO barrier layers with PML processed organic
polymer layers and the transparent dielectric barrier layers are deposited over the plastic or
polymeric substrate. Multilayer structures of such organic and inorganic layers deposited over
a plastic substrate exhibit significantly improved barrier properties as compared to inorganic,
organic or metallic layers alone.

15 In an embodiment, a PML processed top coat polymer layer is applied before the
previously deposited layer contacts a surface, such as a roller, thereby protecting the previously
deposited layer. The PML processed top coat greatly enhances the exclusion of moisture and
atmospheric gases that chemically degrade the display medium and decrease the device
performance, even though the polymer topcoat is not, itself, a good barrier material.

20 Metal oxide dielectric barriers have previously been deposited by evaporation, sputtering,
and chemical vapor deposition processes onto glass substrates. However, for achieving bulk
material-like properties a high temperature deposition method is to be used which melts the
plastic substrate, thereby negatively impacting the mechanical properties of the substrate. In
the present invention, the PML process used for depositing an organic dielectric does not
25 require such high temperatures and therefore does not significantly alter the mechanical
properties of the substrate. However, organic polymer layers alone do not provide substantial
barrier properties, particularly against water vapor.

When TCOs are deposited at low temperatures to accommodate the thermal and
mechanical limits of the substrate, for example, by magnetron sputtering, electron-beam
30 evaporation or plasma enhanced chemical vapor deposition (PECVD), the subsequent TCO
coatings have less than bulk conductivity, i.e. low overall levels of conductivity. TCO films
with a larger thickness deposited through these methods achieve acceptable conductive levels
for portable electronic devices. However, these thick films of TCO are subject to cracking,
crazing and, in some instances, delamination from the substrate, especially when they are
35 processed by a heat treatment step or a coating process involving mechanical rollers (e.g. web
coating). As a consequence, the TCO coating is deposited in a series of thin, separated layers,
yet still maintain high conductive levels. Multiple thin layers of TCO avoid the problems

1 associated with thicker layers, and advantageously are electrically connected in parallel to provide adequate electrical performance characteristics.

5 The thin layers of TCO are preferably deposited in combination with the PML process, which leads to improved optical, electrical and mechanical performance. Superior surface properties (low surface roughness, and high optical quality), barrier properties (low vapor permeability) and mechanical properties result when TCO coatings are deposited by magnetron sputtering on a plastic substrate in combination with the PML process. Preferably, moderate annealing temperature conditions are used for TCO deposition. The resistivity of ITO ("Tin doped indium oxide"), a TCO, is a function of the oxygen and tin content, as well as the deposition conditions (e.g. temperature). Previously, low temperature depositions yielded high resistivity ITO layers, when a low resistivity for ITO was desired. The resistivity of ITO was shown to decrease with a thicker TCO layer. But as discussed previously, thick TCO layers are prone to cracking or crazing. Multiple thin layers of TCO, as described in the present invention, will not crack and will yield a lower resistivity. Moreover, the surface resistivity of a thin film of TCO in multiple layers is low for a given total film thickness, due to its improved microstructure.

15 In an embodiment, a polymer smoothing coating is deposited over the substrate. The smoothing coating is applied by a PML process or liquid coating. A TCO, metal nitride, or metal layer is then deposited over the smoothing layer. Additionally, multiple alternating layers of a protective polymer layer and an additional TCO, metal nitride, or metal layer is deposited. Preferably, the alternating layers are of the same material, e.g. TCO/polymer/TCO, etc.

20 In another embodiment, a polymer smoothing coating layer is optionally deposited over the substrate. Additionally, multiple alternating layers of polymer layers and metal oxide or metal nitride are deposited over the substrate. A TCO layer is then deposited over the top of multiple alternating layers. These multiple alternating layers together with the TCO have adequate barrier and conductivity characteristics.

25 In yet another embodiment, a substrate is coated with a TCO layer, a metal coating, and another TCO layer. This three layer configuration is called "optically enhanced metal," or an induced transmission filter and has similar characteristics as a single TCO layer. With the optically enhanced metal good conductivity, optical transmission and barrier properties are achieved. A similar structure of metal nitrides, e.g., silicon nitride, metal and another metal nitride layer functions equivalently.

30 In still another embodiment, a substrate is alternatively coated with an inorganic layer (such as TCO, metal nitride, or dielectric metal oxides), and polymer layers to provide both barrier and conductive properties.

1 BRIEF DESCRIPTION OF THE DRAWINGS

The aspects of the present invention described above in summary and below in more detail as well as various advantageous aspects will become appreciated as the same becomes better understood with reference to the specification, claims and drawings wherein:

5 FIG. 1 is a cross-sectional view of a composite substrate for a flat panel display (FPD) of the present invention;

FIG. 2 is a cross-sectional view of an embodiment of conductive barrier layer 3 of FIG. 1;

10 FIG. 3 is a cross-sectional view of another embodiment of conductive barrier layer 3 of FIG. 1;

FIG. 4 is a cross-sectional view of another embodiment of conductive barrier layer 3 of FIG. 1;

FIG. 5 is a cross-sectional view of another embodiment of conductive barrier layer 3 of FIG. 1;

15 FIG. 6 is a cross-sectional view of another embodiment of conductive barrier layer 3 of FIG. 1;

FIG. 7 is a cross-sectional view of another embodiment of conductive barrier layer 3 of FIG. 1;

20 FIG. 8 is a schematic illustration of a coating apparatus for forming the conductive barrier layer of FIG. 1;

FIG. 9a is a schematic illustration of a laminating process for the FPD of FIG. 1;

FIG. 9b is a cross-sectional view of the FPD before undergoing a bonding process;

FIG. 9c is a cross-sectional view of the FPD after undergoing a bonding process;

25 FIG. 10 is a chart showing water permeability of an ITO film deposited on a polyethylene terephthalate (PET) substrate versus ITO film sheet resistance;

FIG. 11 is a chart showing water permeability of ITO film deposited on a PET substrate versus ITO film thickness;

FIG. 12 is a chart showing oxygen permeability of ITO film deposited on a PET substrate versus ITO film thickness;

30 FIG. 13 is a chart showing oxygen permeability of ITO film deposited on a PET substrate versus ITO film sheet resistance;

FIG. 14 is a chart showing transmittance and reflectance spectra (for an ITO layer over a silver film layer over an ITO layer over a PET substrate at a sheet resistance of 14 Ohms/Square) versus wavelength;

35 FIG. 15 is a chart showing transmittance and reflectance spectra (for an ITO layer over a PET substrate at a sheet resistance of 29 Ohms/Square) versus wavelength;

FIG. 16 is a chart showing transmittance and reflectance spectra (for an ITO layer over a PET substrate at a sheet resistance of 57 Ohms/Square) versus wavelength;

1 FIG. 17 is a chart showing transmittance and reflectance spectra (for an ITO layer over a PET substrate at a sheet resistance of 65 Ohms/Square) versus wavelength;

FIG. 18 is a chart showing transmittance and reflectance spectra (for an ITO layer over a PET substrate at a sheet resistance of 347 Ohms/Square) versus wavelength;

5 FIG. 19 is a cross-sectional view of an embodiment of a conductive barrier layer;

FIG. 20 is a cross-sectional view of an embodiment of conductive barrier layers of FIG.

1;

FIG. 21 is a cross-sectional view of an embodiment of conductive barrier layers of FIG.

1;

10 FIG. 22 is a cross-sectional view of an embodiment of conductive barrier layers of FIG.

1;

FIG. 23 is a cross-sectional view of an embodiment of conductive barrier layers of FIG.

1;

15 FIG. 24 is a cross-sectional view of an embodiment of conductive barrier layers of FIG.

1;

FIG. 25 is a cross-sectional view of an embodiment of conductive barrier layers of FIG.

1;

FIG. 26 is a cross-sectional view of an embodiment of conductive barrier layers of FIG.

1;

20 FIG. 27 is a cross-sectional view of an embodiment of conductive barrier layers of FIG.

1;

FIG. 28 is a cross-sectional view of an embodiment of conductive barrier layers of FIG.

1;

FIG. 29 is a cross-sectional view of an embodiment of conductive barrier layers of FIG.

25 1;

FIG. 30 is a cross-sectional view of an embodiment of conductive barrier layers of FIG.

1;

FIG. 31 is a cross-sectional view of an embodiment of conductive barrier layers of FIG.

1;

30 FIG. 32 is a cross-sectional view of an embodiment of conductive barrier layers of FIG.

1; and

FIG. 33 is a cross-sectional view of an embodiment of conductive barrier layers of FIG.

1.

35 DETAILED DESCRIPTION OF THE INVENTION

A flat panel display (FPD) 1, of the present invention as shown in FIG. 1, employs lightweight, flexible, plastic substrates 38 for constructing FPDs. In between two plastic substrates of the flat panel display are at least two electrodes. At least one of the electrodes is

1 transparent for viewing of the display. A display medium 2 for the flat panel display is situated between the two electrodes. The display medium, as well as some electrode material, are protected from oxidative degradation and reaction or incorporation of moisture.

5 The displays are fabricated using plastic substrates such as various polyolefins, e.g. polypropylene (PP), various polyesters, e.g. polyethylene terephthalate (PET), and other polymers such as polyethylene naphthalate (PEN), polyethersulphone (PES), polyester carbonate (PC), polyetherimide (PEI), polyarylate (PAR), polyimide (PI), and polymers with trade names ARTON® (Japanese Synthetic Rubber Co., Tokyo, Japan) and AVATREL™ (B.F. Goodrich, Brecksville, Ohio). See Appendix A for deposition temperature capabilities of the particular plastic substrate.

10 In the present invention, at least one layer, a conductive barrier layer 3 has both barrier characteristics (to protect the display medium and/or the metal electrode) and the ability to function as an electrode, and is deposited over the substrate to form a composite substrate, as shown in FIG. 19. In particular, layer 3 has both low oxygen and moisture permeability, and a low enough resistivity to function as an electrode for the display.

15 As shown in the general embodiments of FIGs. 2 through 7, conductive barrier layer 3 comprises at least one sublayer 3' deposited over the substrate, for instance a single ITO layer. In an embodiment, at least one pair of sublayers (a dyad of a polymer and a TCO, metal, or metal oxide) is deposited over the substrate. In an exemplary embodiment, multiple alternating sublayer pairs, comprised of the same materials as the original sublayer pair, are deposited over the substrate or over the previously deposited sublayer.

20 There are a myriad of possibilities for materials comprising the sublayers of the conductive barrier layer. FIGs. 2-7 illustrate generally only some of the more preferred embodiments of sublayer 3' materials for conductive barrier layer 3, while FIGs. 19-33 illustrate particularly the more preferred embodiments for the conductive barrier layer.

25 In an embodiment, a base coating 20 is deposited over the substrate 38. The base coating is a polymer smoothing coating applied by a PML process or an organic hardcoat deposited by a liquid coating process to render a hardcoated PET substrate that is abrasion resistant. A TCO 22 (or metal layer 12) is then deposited over the base coat, as shown in FIG. 3, and more particularly in FIG. 20. Additionally, multiple alternating layers of a protective polymer layer 24 and an additional TCO 22 (or metal layer 12) are additionally deposited, as represented by sublayer 3' in FIG. 3, and more particularly in FIGs. 21 and 22. Preferably, the alternating layers are of the same material, e.g. TCO/polymer/TCO, etc. FIG. 2 illustrates the embodiment of polymer/TCO/polymer without base coat 20. Alternatively, a metal conductor or reflector 12 overlays the top polymer layer 24 as in FIGs. 23-25, and 30.

35 In another embodiment shown in FIG. 26, a substrate is coated with a TCO layer, a metal coating, and another TCO layer. This three layer configuration is called an "optically enhanced metal," and has characteristics similar to a single TCO layer. With the optically enhanced

1 metal, good conductivity, transmission and barrier properties are achieved. Deposited on these
three layers is preferably a polymer layer 24, that is alternating with the three layers.
Alternatively, base coat 20 is deposited over the substrate as shown in FIG. 27. Additionally
5 or alternatively, another dyad (a metal and TCO pair) is deposited over the top TCO layer, as
shown in FIGs. 28 and 29. Additionally or alternatively as shown in FIG. 29, an additional
polymer layer 24 (a polymer overcoat) is deposited over the previously deposited dyad. In
another alternative, a thick metal layer 12 is deposited over the polymer overcoat layer, as also
shown in FIG. 29. Alternatively, a metal nitride layer is substituted for one or more of the metal
layers of these embodiments, for example, see FIGs. 31 and 32.

10 In still another embodiment, a substrate is alternatively coated with an inorganic layer
(such as a TCO or dielectric metal oxides), and polymer layers to provide both barrier and
conductive properties.

FIG. 33 illustrates a metal layer 12 sandwiched between two metal nitride layers 14.
Alternatively, additional dyads (metal and metal nitride pair) are deposited over the metal
15 nitride layer. Further embodiments of this dyad pair are similar to the TCO/ metal dyad pair
embodiments of FIGs. 26-29, i.e. the TCO layers of FIGs. 26-29 are replaced by one or more
metal nitride layers.

In an alternative embodiment, a dielectric layer replaces one or more TCO layers in the
above described embodiments (see generally FIGs. 6 and 7). As shown in FIG. 7, multiple
20 alternating layers of dielectric 17 and polymer layers 24 are deposited over the substrate 38.
The number of multiple alternating layers (or dyads) vary, and is represented here by 3',
sublayers of the conductive barrier layer 3. A TCO layer 22 is then deposited over the top of
multiple alternating layers. These multiple alternating layers together with the TCO have
adequate barrier and conductivity characteristics as described in more detail below.

25 Each TCO layer 22 of the above embodiments is a single TCO layer. Alternatively, the
TCO layer represents two TCO layers.

Preferably, metal layers that are alternating dyad pairs or in between TCO, metal nitride,
or dielectric layers are thin. In addition, metal layers that are adjacent the display matrix, i.e.
overlying the dyad layers, have a greater thickness than the sandwiched metal layers.

30 Sublayer 3' materials that provide barrier properties are thin transparent metal oxides 16,
and/or thin transparent metallic films 12. The polymers 24 enhance barrier properties by
reducing the number of holes and defects in the films upon which or under which they are
deposited. The metal oxide layers alternatively comprise dielectric layers 17 and/or transparent
conductive oxide layers 22. The thickness for these barrier layers are in the nanometer and
35 angstrom range. The thickness for the PML deposited layers are in the micron range. For
example, improved barrier coating occurs when a PML deposited organic polymer layer (a base
coat), and/or a metal oxide layer is placed over the plastic substrate. See Tables 2 and 3.

1 Sublayer 3' materials that provide conductive properties include a thin TCO 22, a thin
transparent metallic film 12 (such as aluminum, silver, copper, gold, platinum, palladium, and
alloys thereof), and a metal nitride 14 (such as transition metal nitrides, for example, titanium
nitride, zirconium nitride, hafnium nitride, and nitrides of Group IVA, VA, and VIA elements
5 of the Periodic Table, as well as nitrides of Group IIIB and IVB elements of the Periodic Table,
for example: gallium nitride, silicon nitride, and aluminum nitride). The thickness for these
conductive layers are in the nanometer and angstrom range. Preferably the TCO is formed by
multiple thin layers deposited with electrical contact to each other, so that a low resistivity is
achieved. Consequently, the TCO functions as both the electrode and a barrier.

10 In the preferred embodiment, there is a PML processed base coat 20 deposited over the
substrate as shown in FIG. 3. The base coat produces substrate smoothing, and more
importantly, in combination with other layers, the base coat has surprisingly effective vapor
barrier enhancement properties because of the smoothing and protection characteristics. The
sublayers are deposited in combination with the process illustrated in FIG. 8.

15 Using a smoothing base coat layer over the plastic substrate imparts good optical and
barrier quality throughout the substrate layers and provides a pristine surface for nucleation of
the deposited TCO electrode layer. The pristine surface smooths over any surface roughness
of the plastic substrate, thereby adding to the FPD lifetime and optical quality.

20 In an exemplary embodiment, one or more metal oxide layers are replaced with a TCO.
When TCO coatings, including ITO ("Tin doped indium oxide"), cadmium oxides (CdSn_2O_4 ,
 CdGa_2O_4 , CdIn_2O_4 , CdSb_2O_6 , CdGeO_4), tin oxides, indium oxides (In_2O_3 ; Ga, GaInO_3 (Sn, Ge),
(GaIn_2O_3), zinc oxides (ZnO(Al) , ZnO(Ga) , ZnSnO_3 , Zn_2SnO_4 , $\text{Zn}_2\text{In}_2\text{O}_3$, $\text{Zn}_3\text{In}_2\text{O}_8$), and/or
magnesium oxides (MgIn_2O_4 , MgIn_2O_4 , $\text{Zn}_2\text{In}_2\text{O}_3$) are deposited on a plastic substrate at a low
temperature, they have an amorphous micro structure. For characteristics of the above TCO
25 materials, see Appendix B. The amorphous structure and oxygen deficiency of the TCO allow
the TCO coating to exhibit conductive properties and barrier properties similar to transparent
dielectric barrier layers, such as types of silica or alumina. Because of the oxygen deficiency,
the barrier layers gather the oxygen and keep the oxygen from passing through. Multiple thin
layers of TCO function as a transparent electrode and a transparent barrier layer. The benefit
30 of using TCO alternating with metallic film layers, besides the barrier properties, is that all the
layers of the structure are conductive; thus improving conductivity.

35 In the preferred embodiment, a suitable apparatus for coating the substrate with
conductive and barrier layers is illustrated schematically in FIG. 8. All of the coating
equipment is positioned in a vacuum chamber 36. A roll of polypropylene, polyester or other
suitable plastic sheet is mounted on a pay-out reel 37. Plastic sheet 38 forming the substrate
is wrapped around a first rotatable drum 39, and fed to a take-up reel 41. A roll 42 is employed,
as appropriate, for guiding the sheet material from the payout reel to the drum and/or to the
take-up reel.

1 A flash evaporator 43 is mounted in proximity to the drum at a first coating station. The
flash evaporator deposits a layer or film of monomer, typically an acrylate, on the substrate
sheet as it travels around the drum. After being coated with a monomer, the substrate sheet
passes an irradiation station where the monomer is irradiated by a source 44 such as an electron
5 gun or source of ultraviolet radiation. The radiation or electron bombardment of the film
induces polymerization of the monomer.

The sheet then preferably passes a sputtering station 46 where a coating of TCO is
applied by magnetron sputtering. The sheet then passes another flash evaporator 47 where
another layer of monomer is deposited over the TCO layer. Depending on whether a layer of
10 monomer is above or below the TCO layer, either evaporator 43 or 47 is used. Clearly, if the
TCO layer is to be sandwiched between layers of polymer, both evaporators and their respective
radiation sources are used. In addition to magnetron sputtering, the TCO layer is processed by
one of thermal evaporation, chemical vapor deposition, plasma enhanced chemical vapor
deposition, and electron beam evaporation. Chemical vapor deposition is a high temperature
15 process, and is therefore the least desirable for use with plastic substrates.

In an alternative embodiment, a liquid PML (called Liquid Multilayer, LML) smoothing
applicator 52 is mounted in proximity to the drum at a first coating station. The liquid
smoothing applicator deposits a layer of monomer, e.g. acrylate, over the substrate. This layer
of monomer is cured by irradiation from an ultraviolet or electron beam source 48 adjacent the
20 drum. Additionally, the sheet then passes sputtering station 46 where a coating of thin metal
film, metal oxide, and/or metal nitride is applied by one of vacuum sputtering, vacuum
metallizing, plasma assisted chemical vapor deposition, or electron beam evaporation. For
example, silicon oxides is deposited by a plasma enhanced chemical vapor deposition process
using a metal organic precursor and an oxidizing or inert carrier gas.

25 The various layers described are deposited in several processes in addition to vacuum
coating techniques. For instance, the layers are deposited through nonvacuum (atmospheric)
roll coating. Alternatively or additionally, the layers are deposited by an in line coating
machine, whereby a conveyor belt runs the substrate to be coated past multiple coating stations.
In a further alternative, the layers are deposited by an intermittent motion machine, that is either
30 in a vacuum process or a nonvacuum process. In yet another alternative, the layers are coated
using a multitude of machines. For instance, the plastic substrate is first coated through
atmospheric roll coating with a cured polymer and subsequently coated by vacuum deposition,
or liquid coated, such as Gravure coating.

35 For multiple layers of organic polymer coatings deposited in the PML process, take up
reel 41, with the sheet wound thereon, functions as the pay out reel 37, and the process is
repeated as desired by coating in both directions. The roll of sheet is removed from the vacuum
system for use.

1 FIG. 9a illustrates a laminating process for the FPD where the coated plastic substrate
and display medium are bonded together with an adhesive, pressure and temperature or through
UV radiation. FIGs. 9b and 9c are a cross-sectional views of the FPD before and after
undergoing the bonding process, respectively. The laminating process is one of the alternate
5 methods for bonding the layers to construct the FPD. Because the layers of the present
invention are thin, cracking, crazing, and delamination are avoided using processing methods
of this type. FIGs. 9b and 9c illustrate the flat panel display with a protective overcoat 4 and
the display medium 2.

10 Transparent dielectric layers with good barrier properties and a high refractive index,
such as metal oxides like titanium oxide or aluminum oxide, or metal nitrides such as silicon
nitride or aluminum nitride, used in combination with thin, transparent metallic film layers
provide a transparent conductive barrier coating. The metal oxide or metal nitride layers are
deposited at specific thicknesses to optimize the optical performance (e.g. transmittance) of a
particular display. Preferably, the thin metallic film layer is sandwiched in between layers of
15 metal oxide or metal nitride. Multiple alternating layers of metal oxides or metal nitrides, with
their barrier properties, and the highly conductive metallic film layers provide increased barrier
performance and conductivity for a particular display medium.

The optical and electrical performance of transparent conductive oxide coatings are also
improved by mildly heating during deposition or post-annealing the coated substrate. Even
20 though the substrate was heated to a moderate temperature of only 65°C, the resistivity of the
ITO was still low enough to effectively operate as an electrode, because of the thin layer of ITO.
See the Experimental Results below.

In an alternative embodiment, a thin conductive metal nitride layer is substituted for one
or more thin metallic film layers. Metal oxide or TCO layers are utilized with the metal nitride
25 layer for enhancing both the optical and electrical performance characteristics. Metal nitrides
have good gas barrier properties. However, to maintain the preferred moisture and oxygen
permeability, there is a minimum thickness of the metal nitride layer. Because of the higher
optical transparency silicon nitride thin films, for example, are attractive candidates for flexible
FPD as barrier layers for atmospheric gases.

30 In another alternative embodiment, at least one of the metallic film layers is replaced
with a polymer layer formed via the PML processes.

RESULTS OF CONDUCTED EXPERIMENTS

35 The plastic substrate for a flat panel display has a very low oxygen and water vapor
permeability, a surface roughness much less than the barrier film thickness, a high Tg (the glass
transition temperature) to allow a higher temperature and/or higher energy ITO deposition
process, and a high transparency with low ND (index of refraction) birefringence.

1 Defects in the coated layers limit the barrier properties. For instance, rough substrates, particulates, and roller contact damage the coated layers. Rough substrates with thin film barriers are smoothed and prevented from damage by roller contact with an organic basecoat and polymer top coat multilayers, respectively.

5 Multiple layers of TCO's deposited on the substrate achieve lower surface resistivity than a single thick layer of TCO. Further, the multiple TCO layers act as electrodes connected in parallel. Using non-stoichiometric dielectric of a group including silicon oxides, aluminum oxides, and silicon nitrides, allow for the fabrication all efficient thin film barriers for flexible plastic films.

10 Measured data for films made of sputtered ITO exhibited exceptional barrier properties. The optical, electrical and barrier properties were measured for ITO sputter-deposited directly onto a PET substrate, and also measured with a PML acrylic base coat over the substrate before deposition of the ITO, in a roll-to-roll (web) coating process. See FIGS. 10-13, and descriptions of the Figures below. The typical performance of a single ITO layer deposited on a base coated PET substrate is $\geq 85\%T$ (Transmittance) and ≤ 80 ohms/square. The ITO layer has a physical thickness of about 140 nm, for a one-half wave optical thickness, while the PET substrate has a thickness of about 0.007". For the single layer ITO film, oxygen permeability ranged from 0.005 to 0.05 oxygen cc/m²/day, while the water permeability ranged from 0.005 to 0.05 g/m²/day.

20 FIG. 10 discloses a chart showing water permeability of ITO film, as well as ITO sandwiching a silver layer, each deposited on a PET substrate versus ITO film resistance. No smoothing base coat was applied to the substrate in either case. First, the ITO layer was DC sputter deposited onto a PET substrate. The deposited ITO film is sputtered from a metal target in a web coater. The vertical lines shown connect the midpoints of the range of permeability results at each measured resistance for the ITO film sheet. The chart shows that the permeability dips to a minimal value of approximately 0.006 g/m² day at a resistance of about 60 ohms/square. The permeability reaches a maximum of approximately 0.21 g/m² day at a resistance of about 350 ohms/square. Second, for a silver layer sandwiched in between ITO film layers over the substrate, the approximate permeability range was 0.04 to 0.075 g/m² day for the sheet resistance at about 12 ohms/square.

30 FIG. 11 discloses a chart showing water permeability of ITO film, as well as ITO sandwiching a silver layer, each deposited on a PET substrate versus ITO film sheet thickness. First, the ITO layer alone is analyzed in the same manner as above. The chart shows that the permeability dips to a minimal value of approximately 0.006 g/m² day at a thickness of about 120 nm. The permeability reaches a maximum of approximately 0.21 g/m² day at a thickness of about 40 nm. Second, for the substrate with the sandwiched silver layer, the approximate permeability range was 0.04 to 0.075 g/m² day for a sheet thickness of approximately 120 nm.

1 FIGs. 12 and 13 disclose charts showing oxygen permeability of ITO film deposited on
a PET substrate versus ITO film sheet thickness and sheet resistivity, respectively. FIG. 12
shows that the permeability dips to a minimal value of approximately $0.017 \text{ g/m}^2 \text{ day}$ at a
thickness of about 220 nm. The permeability reaches a maximum of approximately 0.9 cc/m^2
5 day at a thickness of about 40 nm.

As shown Table 1, alternating barrier layers of PML deposited organic polymers and
dielectrics have permeation rates below the limits of the instruments, which is $0.005 \text{ g/m}^2 \text{ day}$
for Permatran-W 3/31, an instrument for measuring water vapor transmission rates and 0.005
 $\text{cc/m}^2 \text{ day}$ for Ox-Tran 2/20, an instrument for measuring oxygen transmission rates.

10 A transparent dielectric barrier layer or a "single layer" of TCO deposited on the
substrate has suitable barrier properties for the plastic FPD. The preferable barrier properties
vary by the type of display technology: liquid crystal display (LCD) and organic light emitting
display (OLED). The acceptable value of vapor permeation with plastic substrates for FPD
depends on the sensitivity of the specific display technology utilized. For example, the LCD
15 is much less sensitive to vapor permeation than the OLED. For the LCD, oxygen permeability
is preferably in the range of about 0.01 to $0.1 \text{ cc/m}^2 \text{ day}$, while water vapor permeability is
preferably in the range of about 0.01 to $0.1 \text{ g/m}^2 \text{ day}$. For OLED, permeabilities of ≤ 0.001
 $\text{cc/m}^2 \text{ day}$ for oxygen, and $\leq 0.001 \text{ g/m}^2 \text{ day}$ for moisture (water vapor) are preferred.

A polymer OLED and a small molecule OLED describes the two basic technologies for
20 the layer that emits light in the OLED. For polymer OLED's, the light emitting material is
deposited by flow coating, spin coating, gravure coating, meniscus coating, curtain coating or
any common liquid coating or printing techniques. The small molecule OLED is normally
thermally evaporated in a vacuum, but is also processed with nonvacuum coating methods. If
the ITO layer is deposited by nonvacuum processes such as by screen printing, the process of
25 the present invention is entirely nonvacuum. Alternatively, the process of the present invention
takes place by both vacuum and nonvacuum methods. Preferably, the process takes place in
a vacuum both to avoid contamination by particulates, and to avoid moisture and oxygen.
Superior barrier films and other films are provided by the cleaner vacuum process.

As shown in FIGs. 10 and 11 for the LCD, as long as the sheet resistance is below about
30 250 ohms/square , and as long as the ITO film thickness is between about 75 and 225 nm, the
preferred water permeability for the LCD is met. As shown in FIG. 12, the preferred oxygen
permeability for the LCD is met as long as the ITO film thickness is above about 85 nm and as
long as the sheet resistance is below about 150 ohm/square . Because of the lower
permeabilities preferred for the emissive displays (e.g. OLED), the barrier capability is
35 enhanced by multilayer dielectric or TCO barriers in combination with PML processed polymer
coatings (i.e. composite barrier layers of PML deposited organic polymer layers, dielectric
layers and/or TCO layers).

1 Appendix D has two charts that illustrate water vapor and oxygen permeability versus
ITO thickness. The measured results for semi-reactively and reactively sputtered ITO, as well
as the differences between a single ITO layer and two ITO layers (with a polymer layer in
5 between the two layers) made with a semi-reactive process, are illustrated and in tabular form.
'Semi-reactively' sputtered refers to DC magnetron sputtered from a ceramic target. The
differences between the two processes are due to the specific process parameters, and not
inherent to the process type. As shown, for the same thickness, the two ITO layers have higher
conductivity and lower permeability as compared to the single ITO layer. Further, the two ITO
10 layers have higher electrical performance, because the single ITO layer cracks and/or crazes.

10 The preferred thickness for the deposited layers is different for conductivity and barrier
properties. The deposited film is thick in order to have conductive properties. Also, if a film
layer is too thin it will not have adequate barrier properties. The critical thickness for these
layers varies with the material and, to a lesser extent, how the layer is deposited. For ITO, the
critical minimal thickness is about 20 nanometers (or 200 angstroms). The lower limits for
15 some of the metal oxides are about 10 to 30 nanometer range in packaging. Generally, 5-10
nanometers is the minimum thickness for adequate barrier properties. However, enhanced
conductive properties result film thickness in the range of about 20 nanometers to 300
nanometers. If the film is thicker than that range, then the film starts cracking, and hence, loses
conductivity and barrier properties. For maximizing optical transmission, it is well known that
20 optical thicknesses of thin films are selected. The typical physical thickness is 20-300
nanometers for ITO on a flexible substrate.

As seen in FIGS. 15-18, generally, regardless of the sheet resistance, the percentage of
spectral transmittance and reflectance remains relatively constant. For example, at about a
wavelength of 500 nm, the transmittance percentage is about 80% for resistance ranging from
25 29 ohms/square to 347 ohms/square. DC sputter deposited ITO on a hardcoated PET substrate
exhibited a resistivity of 46.9 Ohms/square, which is approximately 5×10^{-4} ohm-cm, and a
visible transmittance of 84.7%. Generally, the transmittance increases (and the reflectance
decreases) as the plasma wavelength increases. There is always a compromise between high
optical transmittance and high conductivity. In contrast, for FIG. 14 (a more preferred
30 embodiment of the present invention), at the higher wavelengths, the transmittance decreases
(and the reflectance increases).

Appendix E illustrates the Transmittance and Reflectance of semi-reactively sputtered
ITO on a PET substrate for various thicknesses versus wavelength. The transmittance and
reflectance of a substrate coated with a polymer layer and an ITO layer, a substrate with an ITO
35 layer, and a substrate with two ITO layers (with a polymer layer in between the two ITO layers)
are illustrated. Generally, transmittance and conductivity are inversely related. Improved
optical performance is achieved by controlling the thickness and index of the polymer layers.

1 For a transparent electrode, conductivity varies with display technology and addressing
method. The surface resistivity for LCD's is about 50-300 Ohm/square, and for OLED's is
about 10-100 Ohm/square. The corresponding visible transmittance for LCD's is about 90%,
and for OLED's is about 80-85%. The thickness of the conductor layer is compatible with the
5 vacuum web coating processing for the flexible plastic substrate.

Table 1 shows the test results for oxygen and water vapor transmission rates of various
samples of a substrate coated with a single ITO layer with different ohm/square coatings and
a substrate coated with an ITO layer, a metal layer, and another ITO layer. The test conditions
were as follows: the temperature was at 23°C/73.4°F. On each side of the barrier for the
10 oxygen transmission rate tests, the relative humidity was 0%. On one side of the barrier for the
water vapor transmission rate tests, the relative humidity was 100%, but the other side of the
barrier had a relative humidity of 0%.

The first eight samples are a single layer ITO with different resistances coated onto a
plastic substrate. For example, the '25-1' is the first sample of the resistance of 25 ohm/square;
15 whereas '25-2' is the second sample from the same lot. The last two samples are of a substrate
coated with an ITO layer, a metal coating, and another ITO layer, with a resistance of 10
ohm/square. This 3 layer configuration is called "optically enhanced metal," or "induced
transmission filter," and has similar characteristics as a single TCO layer. With the optically
enhanced metal good conductivity, transmission and barrier properties are achieved. Preferably
20 the ITO layers, which antireflect the metal, each have a thickness of about 30-60 nanometers.
In several instances, the samples were tested two times. The second column for the 25 and 60
ohm/square reflects the results of the second test.

Table 1

Sample	Water Vapor Transmission Rate (g/m ² *day)		Oxygen Transmission Rate (cc/m ² *day)	
25-1	0.026	<0.005 ¹	0.017	0.087
25-2	0.097	<0.005 ¹	0.584	0.257
60-1	0.042		0.059	0.071
60-2	0.050		0.204	0.090
60-3	0.007		<0.005 ²	
60-4	<0.005 ¹		0.014	
300-1	0.243		0.861	
300-2	0.232		0.864	
M-10-1	0.076		0.035	
M-10-2	0.041		0.024	

¹ The actual water vapor transmission rate was at least as low as the lower limit of the instrument. PermTRAN-W 3/31, 0.005 g/m²*day.

² The actual oxygen transmission rate was at least as low as the lower limit of the instrument. Ox-Tran 2/20, 0.005 cc/m²*day.

Table 2 compares permeation rates for different coatings, including multiple dyad (an acrylate/oxide pair) layers, on polyethylene terephthalate (PET) and oriented polypropylene (OPP) substrates. As shown, a single dyad on a substrate has high permeation resistance for oxygen and moisture. In some instances, two oxygen transmission rate tests were conducted, and the results were shown in a second column. Footnote ¹ denotes the typical permeation rate for the PET substrate.

Table 2

Sample	Water Vapor Transmission Rate (g/m ² *day)	Oxygen Transmission Rate (cc/m ² *day)	
2 mil PET	30.5, 272 ¹ per micron film thickness	5.3, 1550 ¹ per micron film thickness	
Food packaging - target values (PET/oxide)	1.55	1.5	
2 mil PET/single dyad (23°C)	<0.0078	0.03	
2 mil PET/ seven dyads (23°C)	<0.0078	<0.016	
7 mil PET/ hardcoat (23°C)	7.6		
7 mil PET/ hardcoat/ single dyad (38°C)	<0.0078, 90% Relative Humidity (RH), 100% O ₂	0.2682, 100% RH	0.6061, 100% RH
7 mil PET/ hardcoat/ single dyad/ ITO (38°C)	<0.0078, 90% RH, 100% O ₂	0.0098, 100% RH	0.0128, 100% RH
PET/oxide	0.7-1.5	0.15-0.9	
PET/Al	0.6	0.17	
OPP, copolymer, 1 mil	1800	1.3	
OPP/ oxide	17-546	0.08-0.4	
OPP/Al	20	0.11	

Table 3

Sample	Water Vapor Transmission Rate (g/100in ² *24 hours)	Oxygen Transmission Rate (cc/100in ² *24 hours)
A	<0.001	<0.001
B	<0.001	<0.001
C	<0.001	<0.001
D	<0.001	<0.001
E	0.369	1.971
F	0.370	1.934
G	0.340	1.834
H	0.377	1.888

Samples A through D are layers of polymer (PML)/oxide/polymer (PML) on 2 mil PET. Samples E through H are 2 mil PET only.

Although the present invention has been described and is illustrated with respect to various embodiments thereof, it is to be understood that it is not to be so limited, because changes and modifications may be made therein which are within the full intended scope of this invention as hereinafter claimed. In particular, the structure disclosed for flat panel displays is also used with other display technologies, such as polymer light emitting diode (PLED) and light emitting diode (LED) displays.

1 CLAIMS

1. A composite substrate for use in flat panel displays, packaging or electro luminescence lamps comprising:
- 5 a plastic substrate; and
a first conductive barrier material deposited over the plastic substrate, the conductive barrier material including one of a thin transparent conductive oxide, and a metal nitride.
- 10 2. The composite substrate of claim 1 further comprising a first organic polymer deposited over the plastic substrate.
3. The composite substrate of claim 1 further comprising a first organic polymer deposited over the conductive barrier layer.
- 15 4. The composite substrate of claim 2 further comprising a second organic polymer deposited over the conductive barrier layer.
5. The composite substrate of claim 1 further comprising one or more additional layers of conductive barrier material deposited over the plastic substrate, the additional layers of conductive barrier material having the same material as the first conductive barrier material.
- 20 6. The composite substrate of claim 5 further comprising one or more additional layers deposited over the previously deposited conductive barrier material layer, respectively, each additional layer including one of an organic polymer, a thin transparent dielectric, a thin transparent metallic film and a thin transparent conductive oxide.
- 25 7. The composite substrate of claim 1 wherein the thin transparent metallic film is aluminum.
- 30 8. The composite substrate of claim 1 wherein the thin transparent metallic film is silver.
9. The composite substrate of claim 1 wherein the plastic substrate is one of a polyester and a polyolefin.
- 35 10. The composite substrate of claim 1 wherein the transparent conductive oxide coating is tin doped indium oxide.

- 1 11. The composite substrate of claim 1 wherein the transparent dielectric barrier is one of silicon oxide and aluminum oxide.
- 5 12. The composite substrate of claim 11 wherein the aluminum oxide is deposited by one of evaporation of the aluminum which is then converted to an oxide in an oxygen plasma and electron beam evaporation.
- 10 13. The composite substrate of claim 1 wherein the dielectric layer is deposited by a plasma assisted chemical vapor deposition process using one of an oxidizing carrier gas and inert carrier gas.
14. The composite substrate of claim 7 wherein the aluminum layer is deposited by one of vacuum metallizing and sputtering.
- 15 15. The composite substrate of claim 1 further comprising multiple alternating layers of vapor deposited crosslinked organic monomer, and transparent conductive oxide.
- 20 16. An apparatus for fabricating a composite substrate for use in flat panel display packaging comprising one of a roll coater, a vacuum coater, an in line coating machine and an intermittent motion machine and a Gravure coating machine.
17. The apparatus of claim 16 wherein the substrate is coated using more than one apparatus.
- 25 18. A process for fabricating a composite substrate for use in flat panel display packaging comprising:
 providing a plastic substrate; and
 depositing a first conductive barrier material over the plastic substrate, the
30 conductive barrier material including one of a thin transparent conductive oxide, and a metal nitride.
19. The process of claim 18 further comprising depositing a first organic polymer over the plastic substrate.
- 35 20. The process of claim 18 further comprising depositing a first organic polymer over the conductive barrier layer.

- 1 21. The process of claim 19 further comprising depositing a second organic polymer
over the conductive barrier layer.
- 5 22. The process of claim 18 further comprising depositing one or more additional
layers of conductive barrier material over the plastic substrate, the additional layers of
conductive barrier material having the same material as the first conductive barrier material.
- 10 23. The composite substrate of claim 22 further comprising depositing one or more
additional layers over the previously deposited conductive barrier material layer, respectively,
each additional layer including one of an organic polymer, a thin transparent dielectric, a thin
transparent metallic film and a thin transparent conductive oxide.
- 15 24. The process of claim 19 further comprising vapor depositing and crosslinking an
organic monomer to form the polymer layer.
- 20 25. The process of claim 19 further comprising liquid smoothing an organic polymer
to form the polymer layer.
- 25 26. The process of claim 19 further comprising depositing the polymer layer over the
previously deposited layer before the previously deposited layer contacts a surface.
27. The process of claim 18 wherein the thin transparent metallic film is aluminum.
28. The process of claim 18 wherein the thin transparent metallic film is silver.
29. The process of claim 18 wherein the plastic substrate is one of a polyester and a
polyolefin.
- 30 30. The process of claim 18 wherein the transparent conductive oxide coating is tin
doped indium oxide.
31. The process of claim 18 wherein the transparent dielectric barrier is one of silicon
oxide and aluminum oxide.
- 35 32. The process of claim 31 further comprising depositing the aluminum oxide by one
of evaporation of the aluminum which is then converted to an oxide in an oxygen plasma and
electron beam evaporation.

1 33 The process of claim 18 further comprising depositing the dielectric layer by a
plasma assisted chemical vapor deposition process using one of an oxidizing carrier gas and
inert carrier gas.

5 34. The process of claim 27 further comprising depositing the aluminum layer by one
of vacuum metallizing and sputtering.

 35. The process of claim 18 wherein the transparent conductive oxide is deposited by
sputtering.

10 36. The process of claim 35 further comprising providing hydrogen in a plasma of a
vacuum chamber used in the sputtering process of the transparent conductive oxide.

 37. The process of claim 18 further comprising mildly annealing the substrate before
15 deposition of layers thereon.

 38. The process of claim 37 wherein the substrate is annealed to approximately 65°C.

20

25

30

35

AMENDED CLAIMS

[received by the International Bureau on 25 April 2000 (25.04.00);
original claims 1-3, 5, 8, 11-16, 18-22, 24-29, 31-34 and 36 amended;
original claims 37 and 38 cancelled; new claims 37-41 added;
remaining claims unchanged (5 pages)]

1. A composite substrate for use in one of displays, packaging and electro
luminescence lamps comprising:
5 a plastic substrate;
 a first conductive barrier material deposited over the plastic substrate, the
conductive barrier material including one of a thin transparent conductive oxide, a thin
transparent metal and a thin transparent metal nitride; and
 a first organic polymer deposited over the conductive barrier material.
10
2. A composite substrate for use in one of displays, packaging and electro
luminescence lamps comprising:
 a substrate;
 a first organic polymer deposited over the substrate; and
15 a first conductive barrier material deposited over the first organic polymer layer,
the conductive barrier material including one of a thin transparent conductive oxide, a thin
transparent metal and a thin transparent metal nitride.
3. The composite substrate of claim 1 further comprising a second organic polymer
20 deposited over the plastic substrate, in between the substrate and the conductive barrier layer.
4. The composite substrate of claim 2 further comprising a second organic polymer
 deposited over the conductive barrier layer.
5. The composite substrate of claim 1 further comprising one or more additional
25 layers of conductive barrier material deposited over the first organic polymer layer, the
additional layers of conductive barrier material having the same material as the first conductive
barrier material.
6. The composite substrate of claim 5 further comprising one or more additional
30 layers deposited over the previously deposited conductive barrier material layer, respectively,
each additional layer including one of an organic polymer, a thin transparent dielectric, a thin
transparent metallic film and a thin transparent conductive oxide.
7. The composite substrate of claim 1 wherein the thin transparent metallic film is
35 aluminum.

- 1 8. The composite substrate of claim 1 wherein the thin transparent metallic film is
one of silver, gold, a silver alloy and a gold alloy.
- 5 9. The composite substrate of claim 1 wherein the plastic substrate is one of a
polyester and a polyolefin.
10. The composite substrate of claim 1 wherein the transparent conductive oxide
coating is tin doped indium oxide.
- 10 11. The composite substrate of claim 1 further comprising a first transparent dielectric
barrier which is one of silicon oxide and aluminum oxide.
12. The composite substrate of claim 11 wherein the aluminum oxide is deposited by
one of thermal evaporation of and electron beam evaporation of the aluminum which is then
15 converted to an oxide by an oxygen containing plasma.
13. The composite substrate of claim 11 wherein the dielectric layer is deposited by
a plasma assisted chemical vapor deposition process.
- 20 14. The composite substrate of claim 8 wherein the metallic layer is deposited by one
of vacuum metallizing and sputtering.
15. The composite substrate of claim 1 further comprising multiple alternating layers
of deposited crosslinked organic monomer, and transparent conductive oxide.
- 25 16. An apparatus for fabricating a composite substrate for use in one of display
fabrication and packaging comprising at least one of a roll coater, a vacuum coater, an in-line
coating machine and an intermittent motion machine, and a Gravure coating machine.
- 30 17. The apparatus of claim 16 wherein the substrate is coated using more than one
apparatus.
18. A process for fabricating a composite substrate for use in one of display
fabrication and packaging comprising:
35 providing a substrate;
 depositing a first conductive barrier material over the substrate, the conductive
barrier material including one of a thin transparent conductive oxide, a thin transparent metallic
film and a thin conductive metal nitride; and

1 depositing a first organic polymer over the first conductive barrier layer.

19. The process of claim 18 further comprising depositing a second organic polymer
over the substrate, in between the substrate and the first conductive barrier material.

5

20. The process of claim 19 further comprising depositing one or more additional
layers of conductive barrier material over the first organic polymer layer, the additional layers
of conductive barrier material having the same material as the first conductive barrier material.

10

21. The process of claim 20 further comprising depositing one or more additional
layers over the previously deposited conductive barrier material layer, respectively, each
additional layer including one of an organic polymer, a thin transparent dielectric, a thin
transparent metallic film and a thin transparent conductive oxide.

15

22. The process of claim 18 further comprising depositing one or more additional
layers of conductive barrier material over the first organic polymer layer, the additional layers
of conductive barrier material having the same material as the first conductive barrier material.

20

23. The composite substrate of claim 22 further comprising depositing one or more
additional layers over the previously deposited conductive barrier material layer, respectively,
each additional layer including one of an organic polymer, a thin transparent dielectric, a thin
transparent metallic film and a thin transparent conductive oxide.

25

24. The process of claim 18 further comprising depositing and crosslinking an organic
monomer in one of a vacuum and a plasma to form the polymer layer.

30

25. The process of claim 18 wherein the substrate is a plastic substrate, the process
further comprising smoothing the plastic substrate by depositing a polymer which is liquid
coated over the substrate.

26. The process of claim 18 further comprising depositing the polymer layer over the
previously deposited layer before the previously deposited layer contacts a surface.

35

27. The process of claim 18 wherein the thin transparent metallic film is one of silver,
gold, a silver alloy and a gold alloy.

28. The process of claim 18 wherein the thin transparent metallic film is aluminum.

- 1 29. The process of claim 18 wherein the substrate contains one of at least a polyester
and a polyolefin.
- 5 30. The process of claim 18 wherein the transparent conductive oxide coating is tin
doped indium oxide.
31. The process of claim 18 further comprising depositing a first transparent
dielectric barrier which is one of silicon oxide and aluminum oxide.
- 10 32. The process of claim 31 wherein the aluminum oxide is made by one of thermal
evaporation of and electron beam evaporation of the aluminum which is then converted to an
oxide by an oxygen containing plasma.
- 15 33. The process of claim 18 wherein the transparent conductive oxide layer is
deposited by a plasma assisted chemical vapor deposition process.
34. The process of claim 18 wherein the metallic film layer is deposited by one of
vacuum metallizing and sputtering.
- 20 35. The process of claim 18 wherein the transparent conductive oxide is deposited by
sputtering.
36. The process of claim 35 wherein in the sputtering process of the transparent
conductive oxide, hydrogen is provided in the plasma.
- 25 37. The composite substrate of claim 1 wherein the transparent conductive oxide
coating contains indium.
38. The composite substrate of claim 1 further comprising one or more additional
30 layers of conductive barrier material deposited over the plastic substrate, the additional layers
of conductive barrier material having material that is different than that of the first conductive
barrier material.
- 35 39. The process of claim 18 wherein the transparent conductive oxide coating
contains indium.

1 40. A composite substrate for use in one of displays, packaging and electro
luminescence lamps comprising:

 a plastic substrate; and

5 a first optically enhanced layer deposited over the plastic substrate, wherein the
optically enhanced layer has one of a metal and a metal nitride layer sandwiched between two
thin transparent conductive oxide layers.

10 41. The composite substrate of claim 40 wherein a second optically enhanced layer
is deposited over the first optically enhanced layer, wherein the second optically enhanced layer
has the same material as the first optically enhanced layer.

15

20

25

30

35

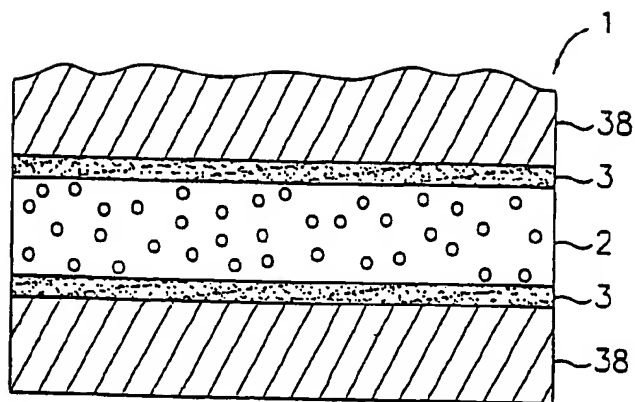


FIG. 1

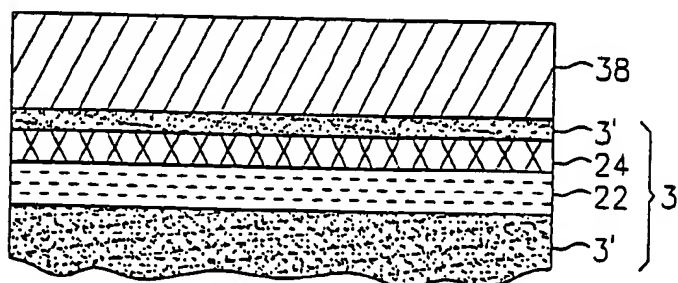


FIG. 2

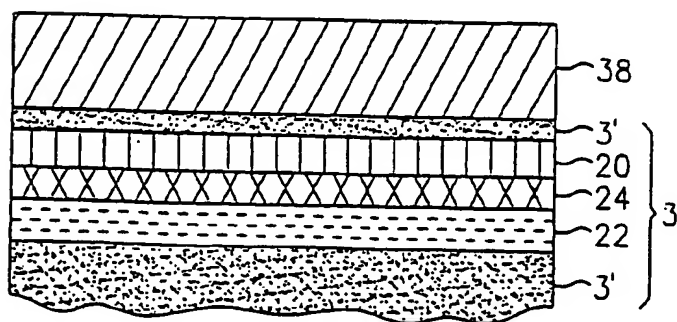


FIG. 3

2/19

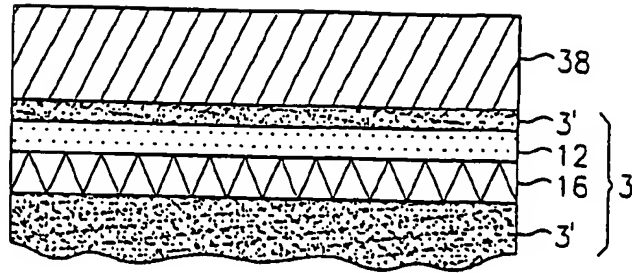


FIG. 4

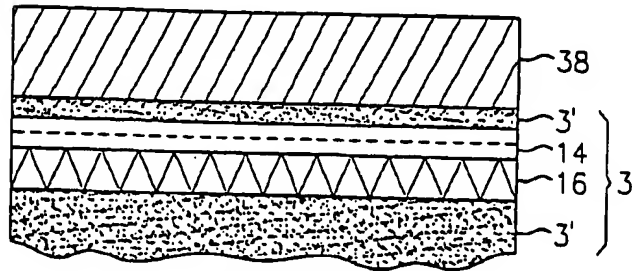


FIG. 5

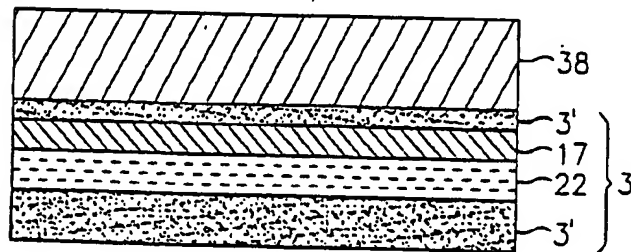


FIG. 6

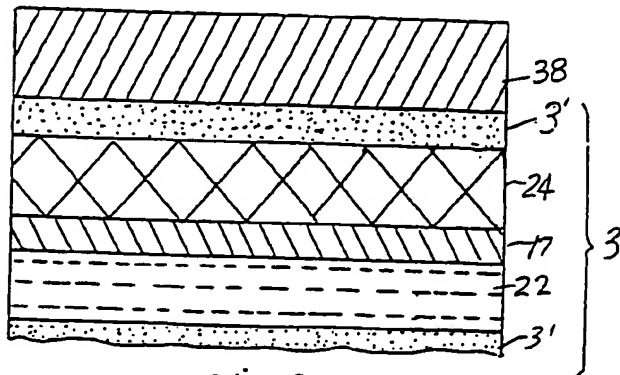


Fig. 7

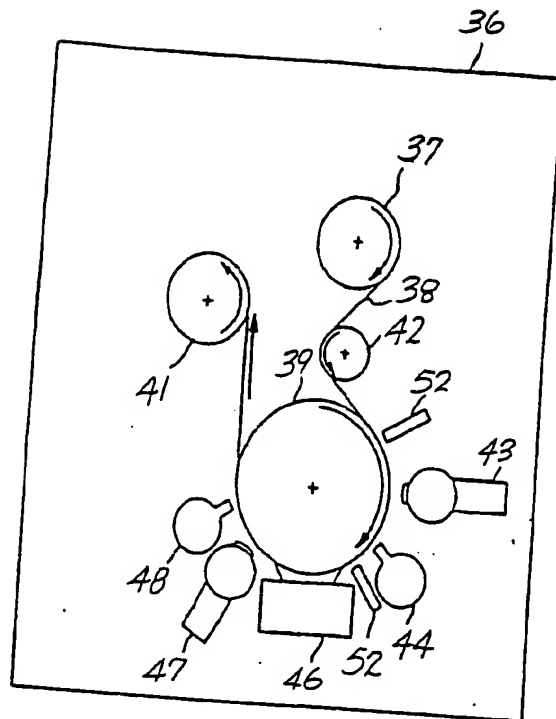


Fig. 8

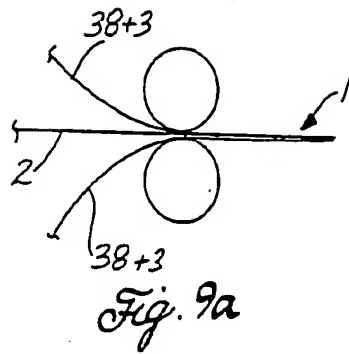


Fig. 9b

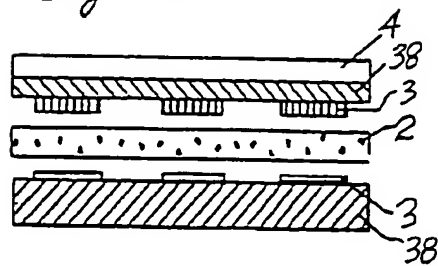
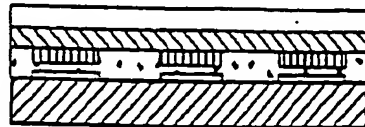
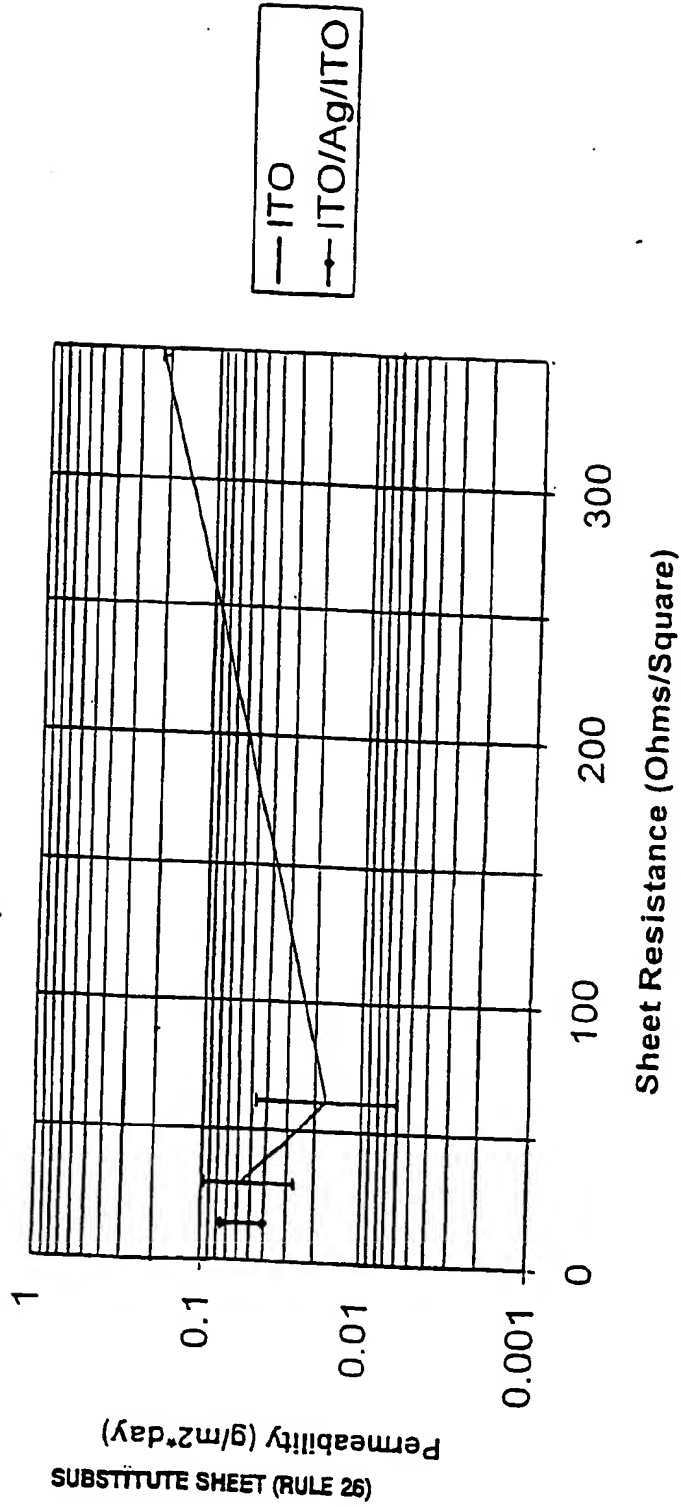


Fig. 9c

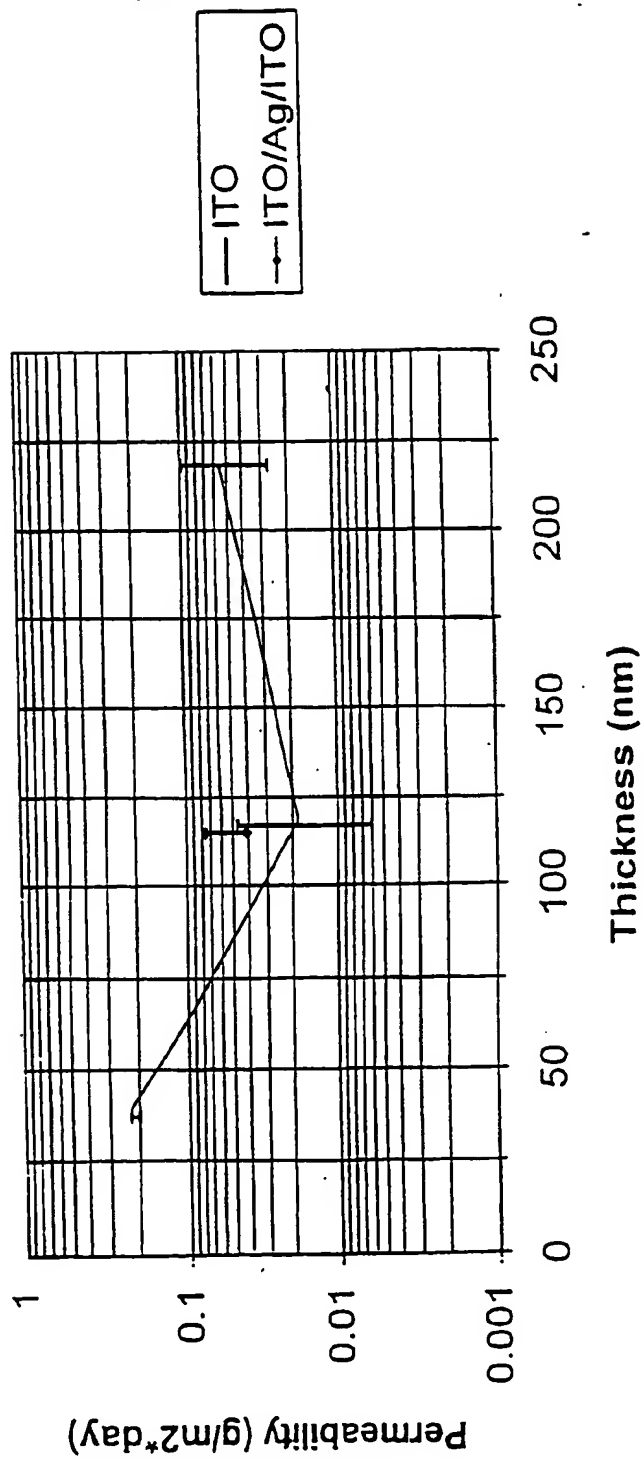


5/19

Fig. 10



6/19

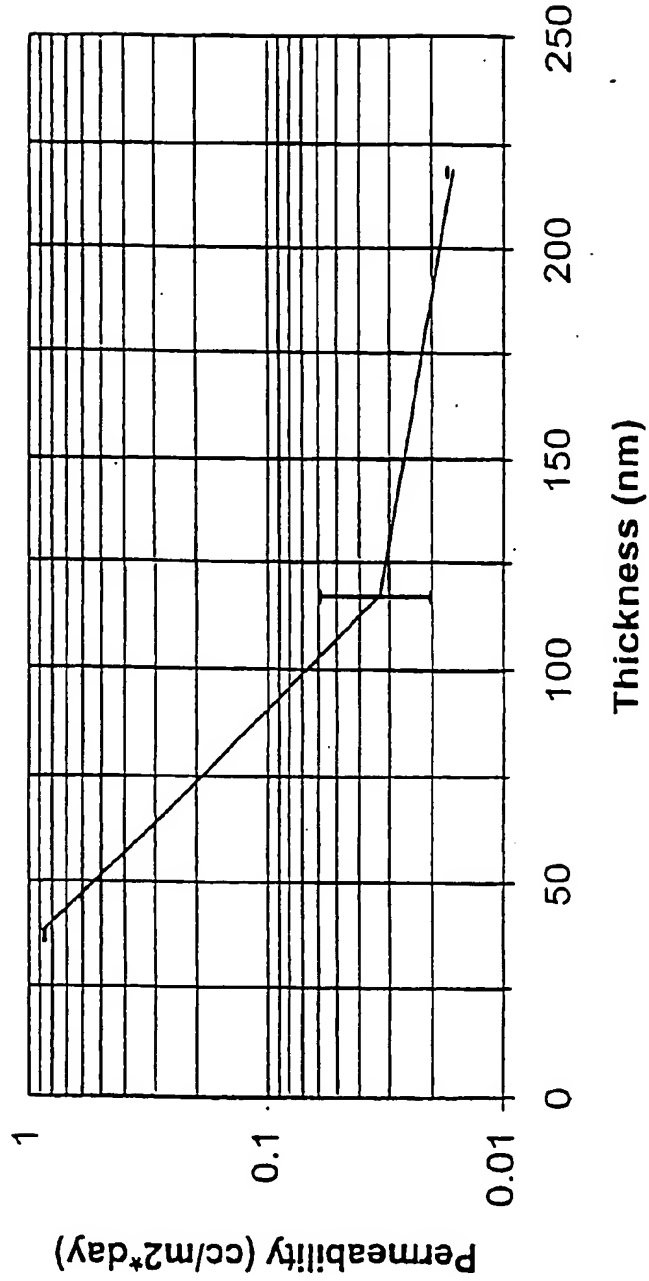
Fig. 11

SUBSTITUTE SHEET (RULE 26)

7/19

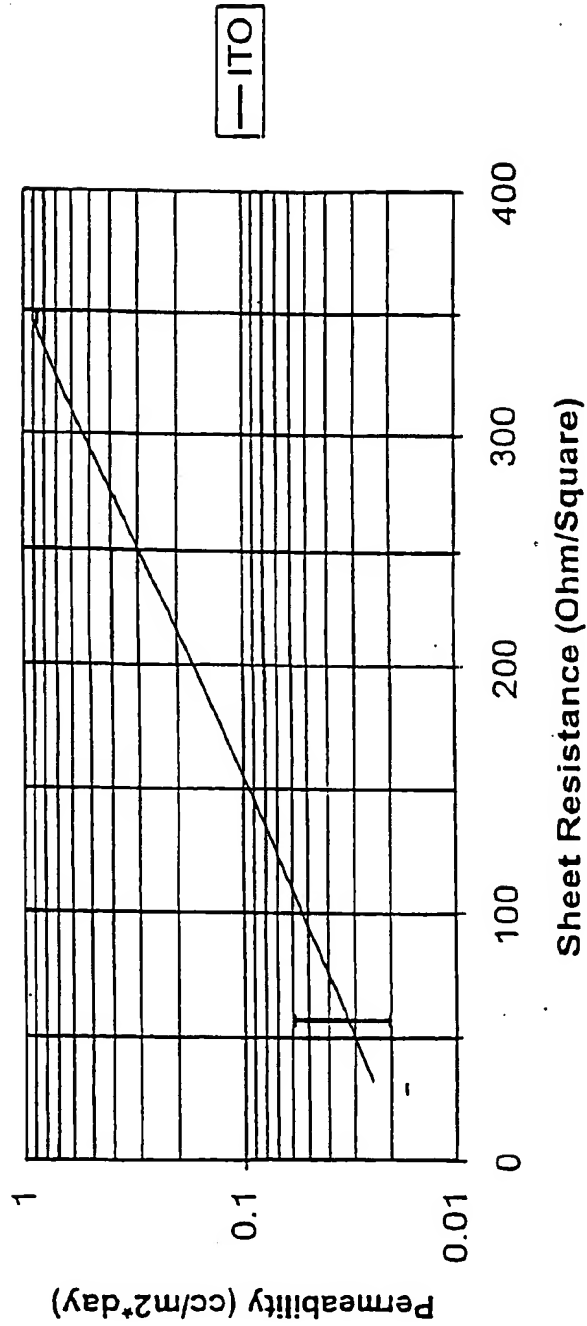
Fig. 12

—ITO



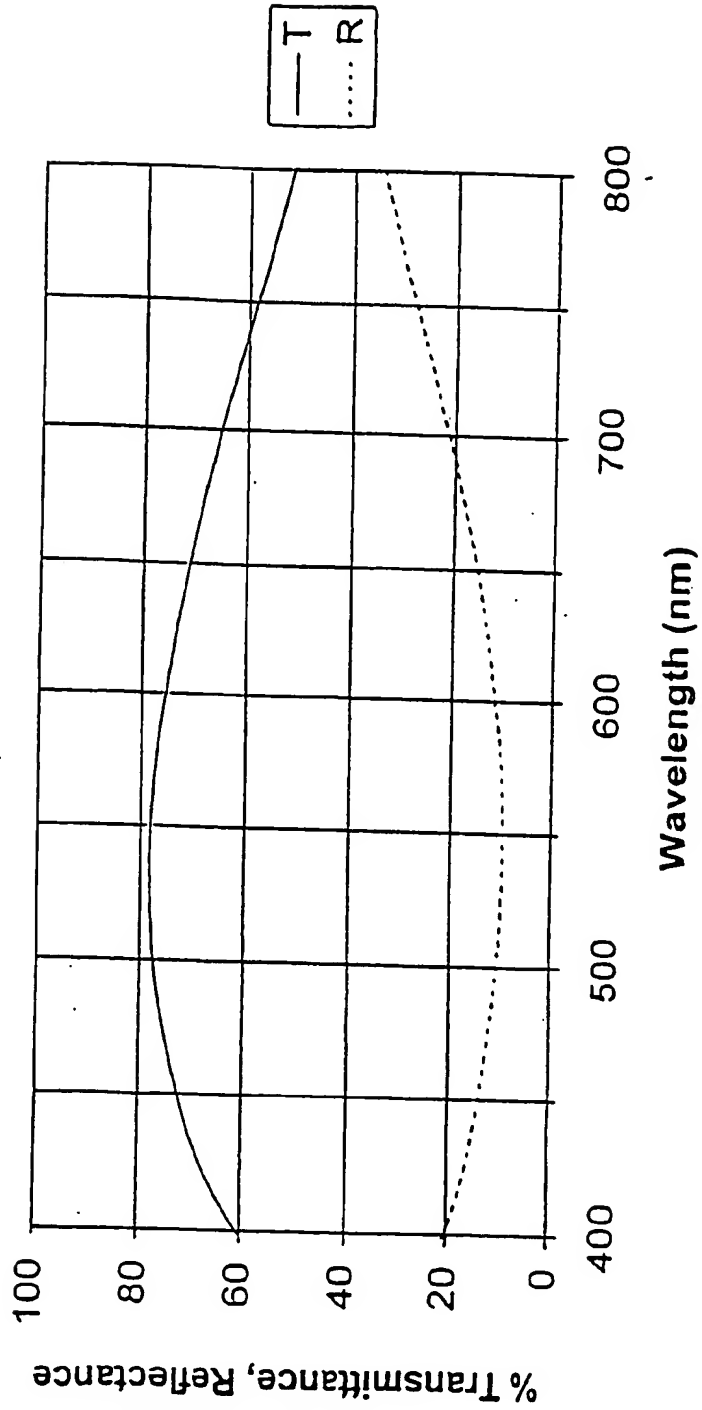
8/19

Fig. 13



9/19

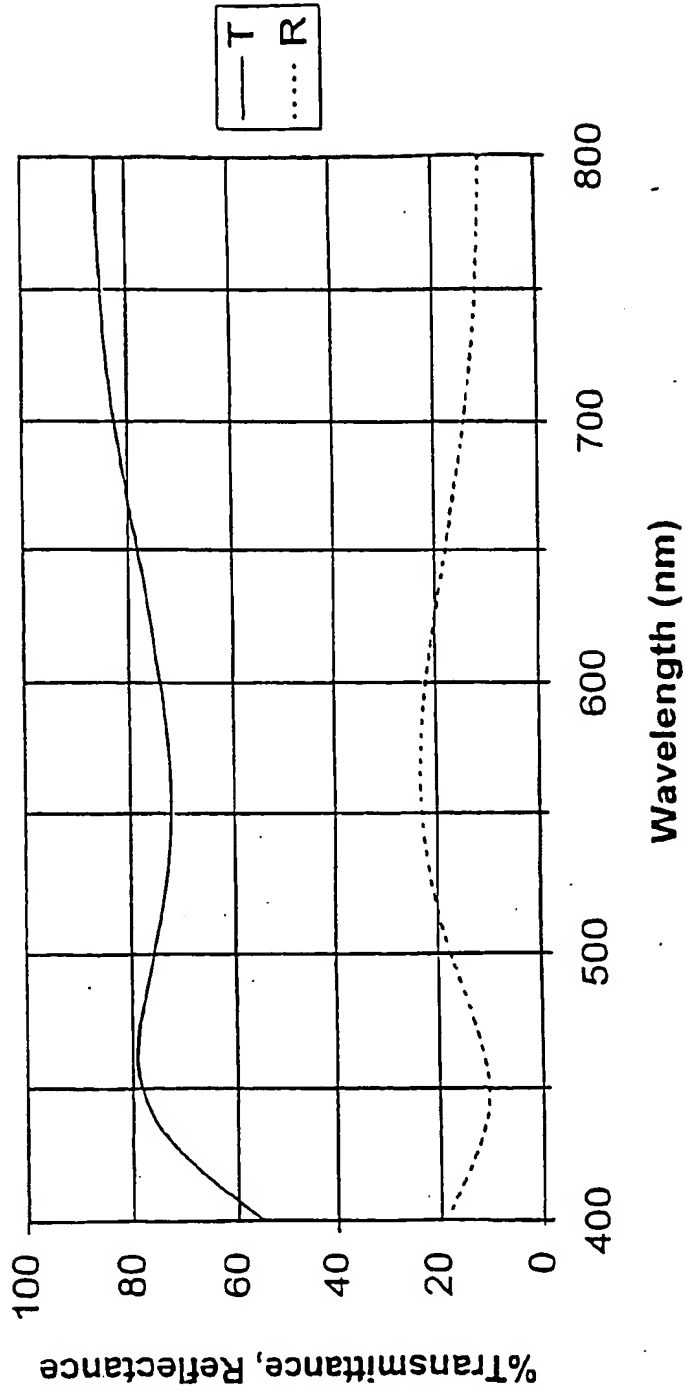
Fig. 14



SUBSTITUTE SHEET (RULE 26)

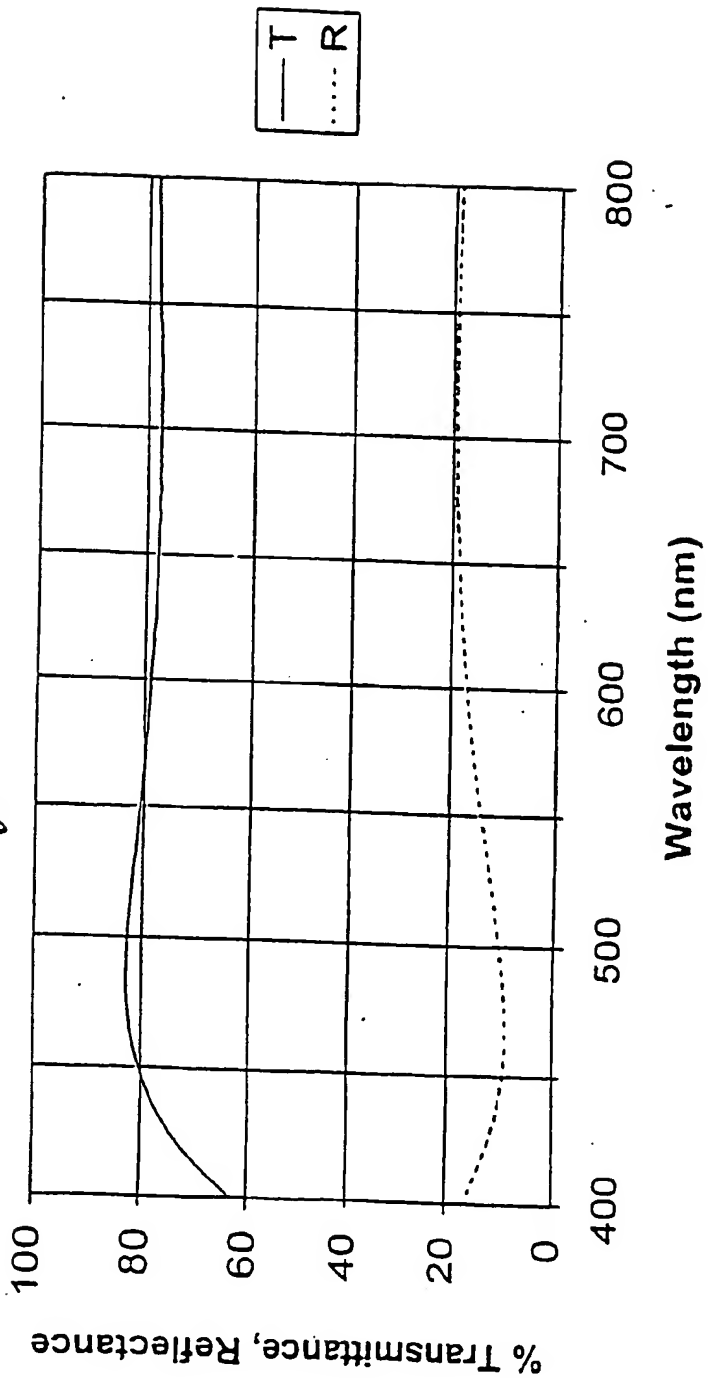
10/19

Fig. 15



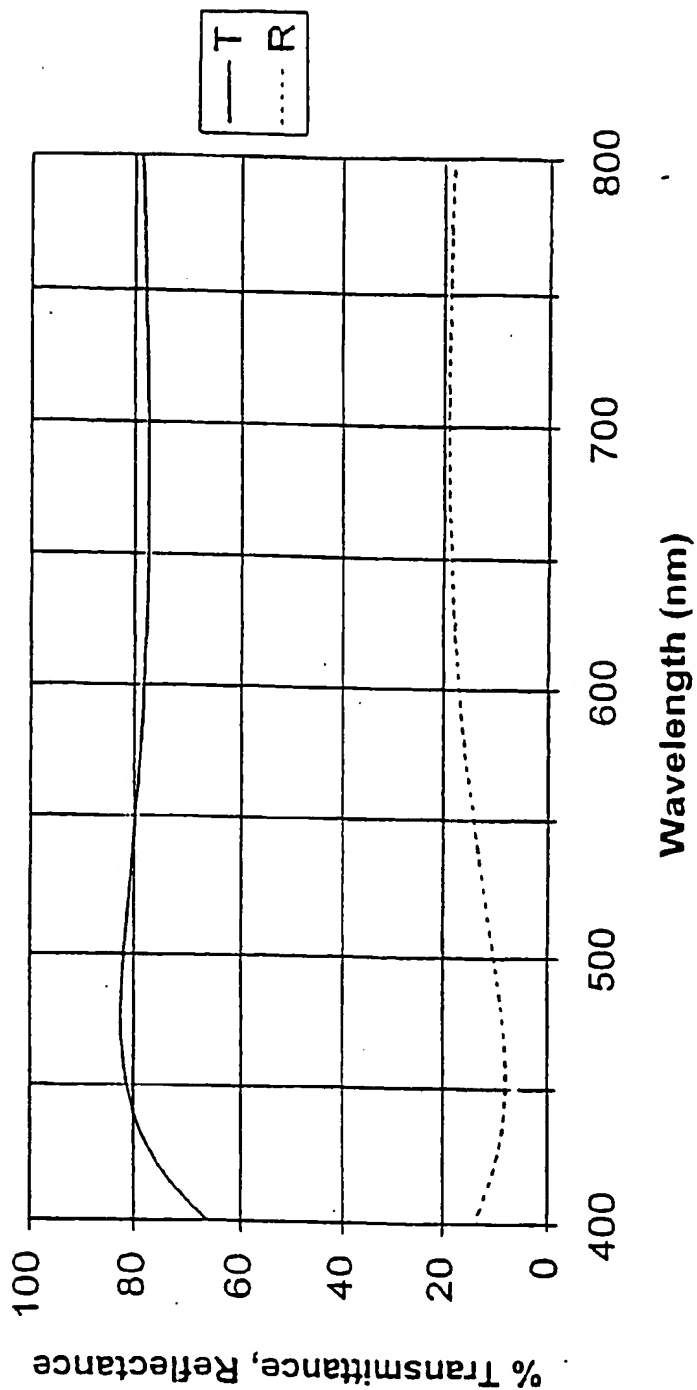
11/19

Fig. 16



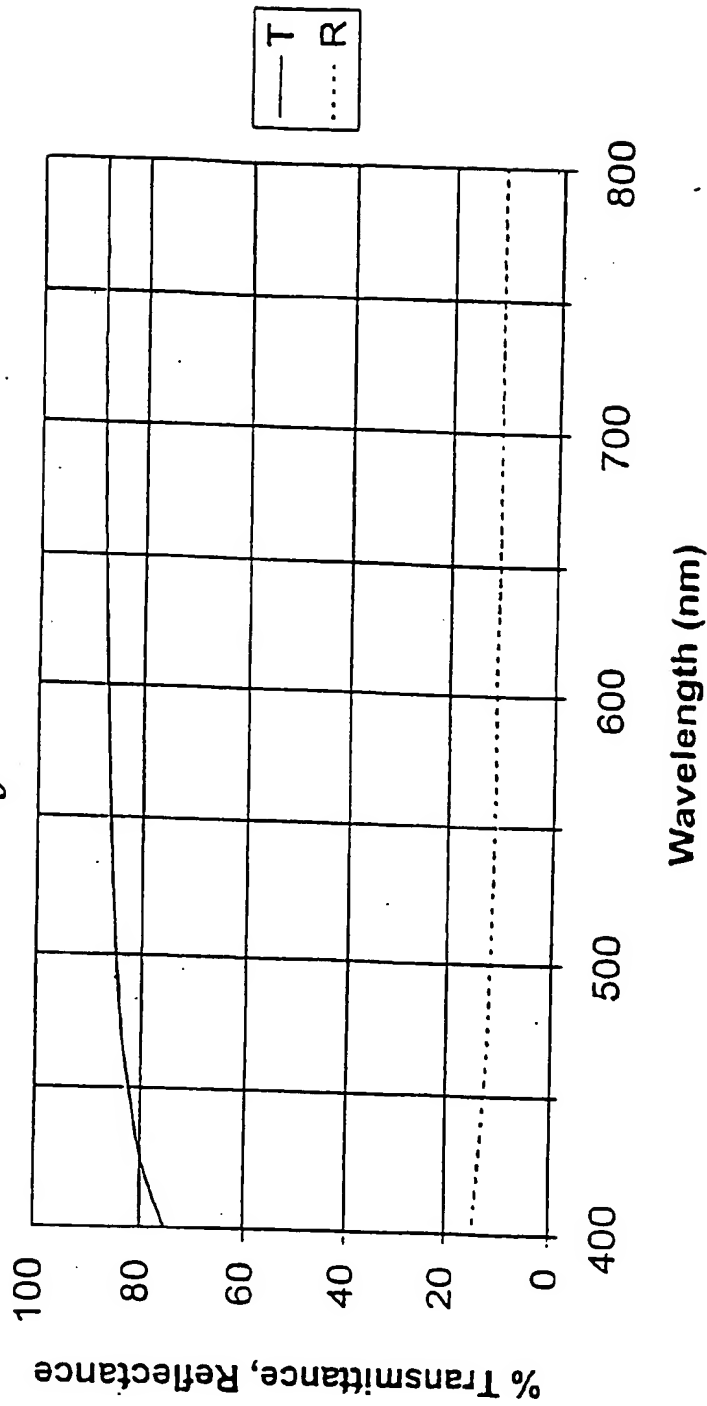
12/19

Fig. 17



13/19

Fig. 1B



SUBSTITUTE SHEET (RULE 26)

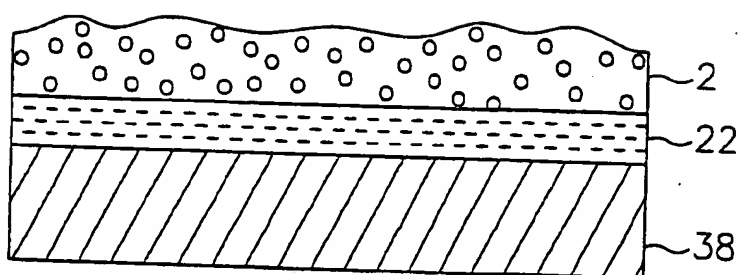


FIG. 19

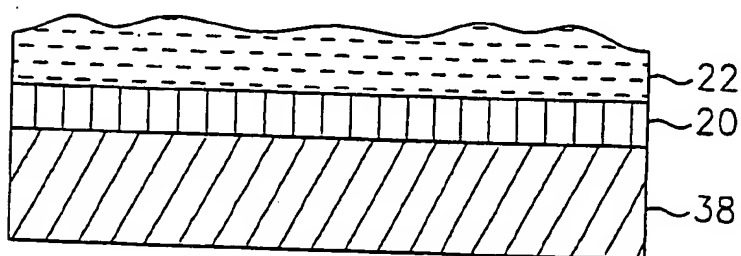


FIG. 20

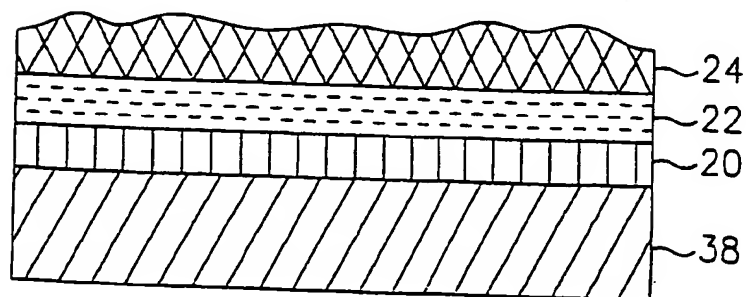


FIG. 21

SUBSTITUTE SHEET (RULE 26)

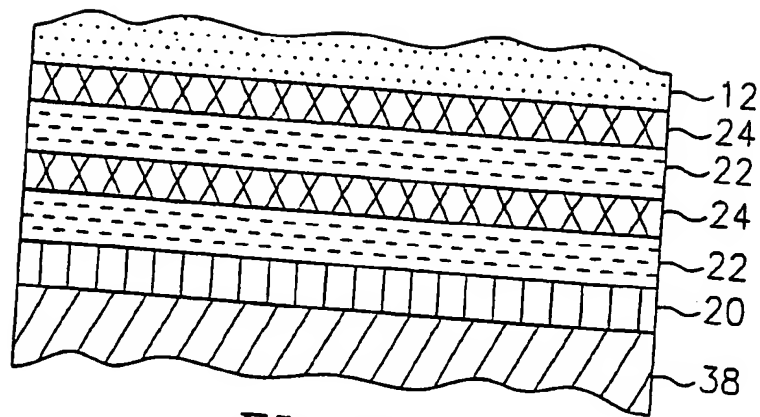


FIG. 25

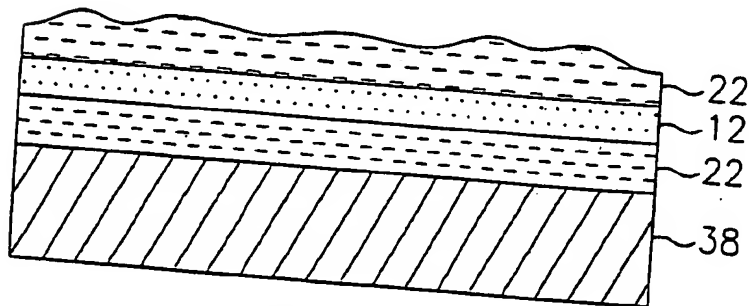


FIG. 26

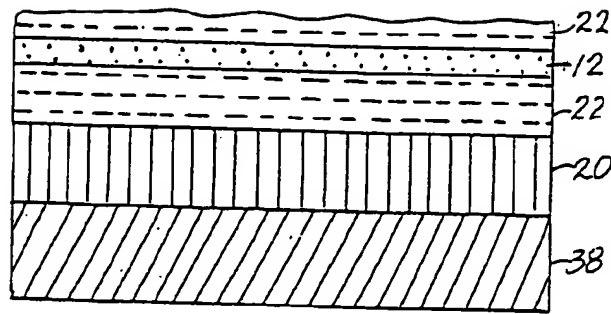


FIG. 27

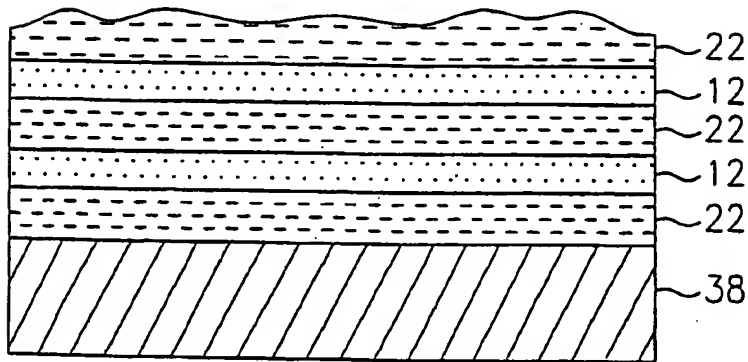


FIG. 28

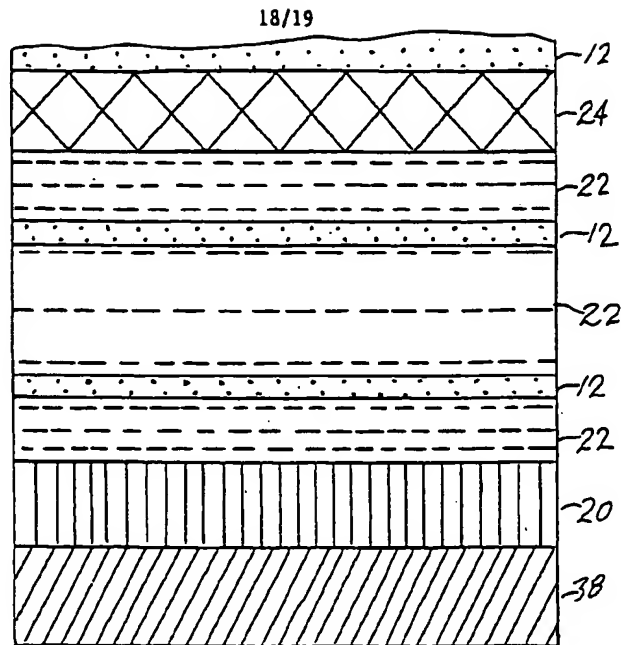


FIG. 29

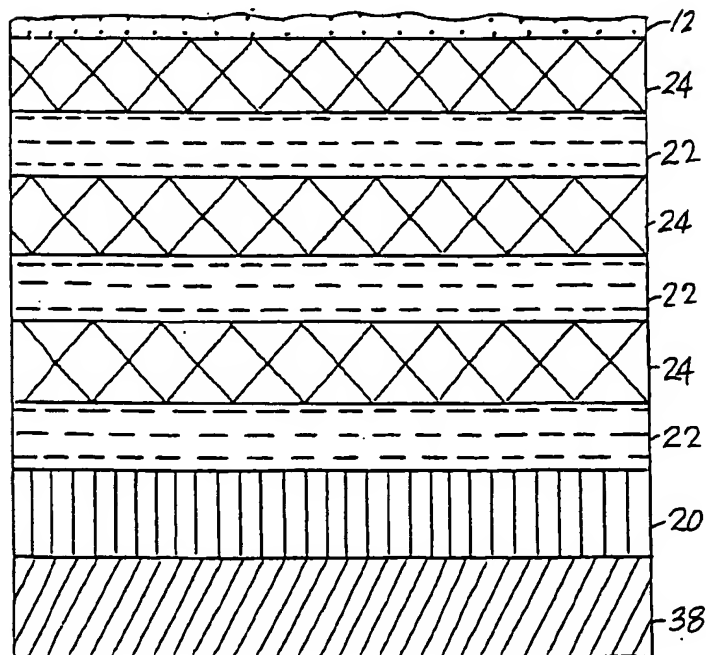


FIG. 30

19/19

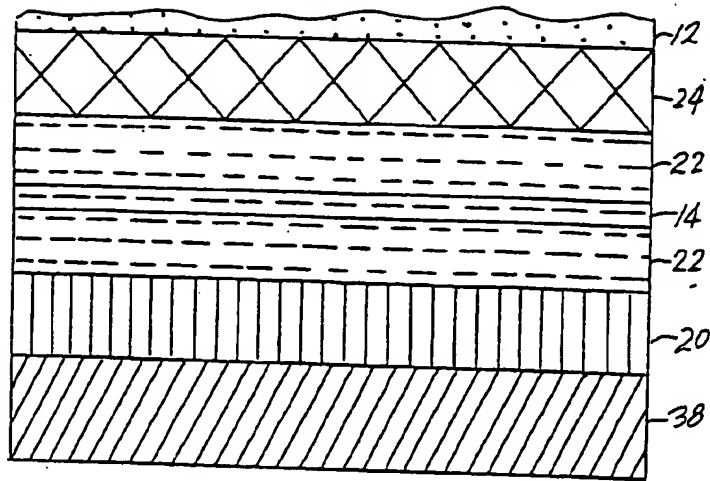


FIG. 31

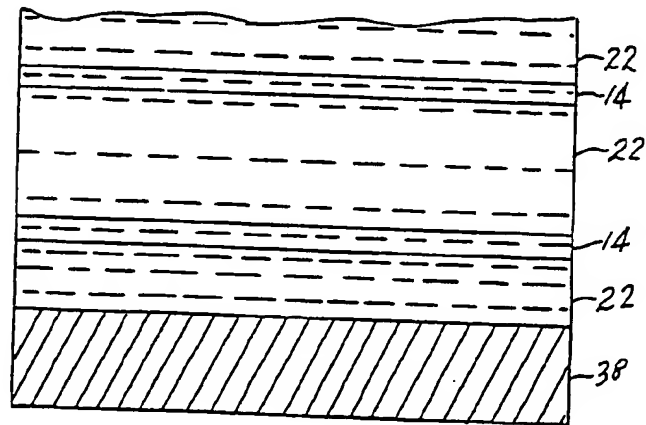


FIG. 32

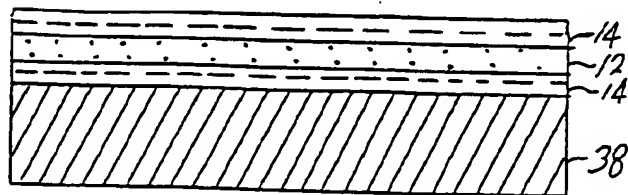


FIG. 33

INTERNATIONAL SEARCH REPORT

Form No. 1/1992

PCT/US 99/25843

A. CLASSIFICATION OF SUBJECT MATTER
IPC 7 H01L51/20 H05B33/04

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 7 H01L 602F H05B

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	PATENT ABSTRACTS OF JAPAN vol. 1998, no. 03, 27 February 1998 (1998-02-27) - & JP 09 291356 A (ASAHI GLASS CO LTD), 11 November 1997 (1997-11-11) abstract	1,5,6,8, 18,22, 23,28
X	PATENT ABSTRACTS OF JAPAN vol. 018, no. 641 (E-1639), 6 December 1994 (1994-12-06) - & JP 05 251631 A (KANEGAFUCHI CHEM IND CO LTD), 9 September 1994 (1994-09-09) abstract	1,9,10, 18,29, 30,35
	-/-	

☒ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

* Special categories of cited documents:

"A" document defining the general state of the art which is not considered to be of particular relevance

"E" earlier document but published on or after the international filing date

"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art

"Z" document number of the same patent family

Date of the actual completion of the international search

17 February 2000

Date of mailing of the international search report

28/02/2000

Name and mailing address of the ISA

European Patent Office, P.O. Box 5018, D-69110 Heidelberg 2,
NL - 2280 HV Rijswijk
Tel. (+31-70) 340-2060, Tx 31 651 epo nl,
Fax (+31-70) 340-3018

Authorized officer

De Laere, A

INTERNATIONAL SEARCH REPORT

Date of application No
PCT/US 99/25843

C. (Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT		
Category	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	PATENT ABSTRACTS OF JAPAN vol. 016, no. 582 (E-1300), 22 December 1992 (1992-12-22) -A JP 04 230906 A (UNITIKA LTD), 19 August 1992 (1992-08-19) abstract	1,9,10, 18,29,30
X	DATABASE WPI Section Ch, Week 198744 Derwent Publications Ltd., London, GB; Class A85, AN 1987-309622 XP002130779 -A JP 62 217506 A (UNITIKA LTD), 25 September 1987 (1987-09-25) abstract	1,9,10, 18,29, 30,35
A	AFFINITO J D ET AL: "A NEW METHOD FOR FABRICATING TRANSPARENT BARRIERS LAYERS" THIN SOLID FILMS, CH, ELSEVIER-SEQUOIA S.A. LAUSANNE, vol. 290/291, 15 December 1996 (1996-12-15), pages 63-67, XP000693807 ISSN: 0040-6090 the whole document	1-6,9, 15,16, 18-26,29
A	US 5 547 508 A (AFFINITO JOHN D) 20 August 1996 (1996-08-20) cited in the application column 6, line 5-7; claims	1-6,10, 15-22, 24-26, 30,35
A	EP 0 260 626 A (TOYO BOSEKI ;FUJIMORI KOGYO CO (JP)) 23 March 1988 (1988-03-23) page 6, line 10-32	1,5,10, 18,22, 30,35
A	US 5 757 126 A (HARVEY III THOMAS B ET AL) 25 May 1998 (1998-05-26) the whole document	1-6, 9-11, 18-23, 29-31,35
A	WO 92 12219 A (MINNESOTA MINING & MFG) 23 July 1992 (1992-07-23) page 29, line 27 -page 30, line 11	1,6, 9-11,18, 23, 29-31,35
E	EP 0 977 469 A (HEWLETT PACKARD CO) 2 February 2000 (2000-02-02) the whole document	1-4,9, 10, 18-21, 24-26, 29,30,35

Form PCT/ISA/210 (continuation of second sheet) (July 1992)

INTERNATIONAL SEARCH REPORT

information on patent family members

International Application No.
PCT/US 99/25843

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
JP 09291356 A	11-11-1997	NONE	
JP 06251631 A	09-09-1994	NONE	
JP 04230906 A	19-08-1992	NONE	
JP 62217506 A	25-09-1987	NONE	
US 5547508 A	20-08-1996	US 5395644 A US 5260095 A AT 170779 T CA 2142895 A DE 69320971 D DE 69320971 T EP 0655954 A JP 8503099 T WO 9404285 A	07-03-1995 09-11-1993 15-09-1998 03-03-1994 15-10-1998 27-05-1999 07-06-1995 02-04-1996 03-03-1995
EP 0260626 A	23-03-1988	JP 2632673 B JP 63071829 A DE 3788391 D DE 3788391 T KR 9008063 B US 4802742 A	23-07-1997 01-04-1988 20-01-1994 21-04-1994 31-10-1990 07-02-1989
US 5757126 A	26-05-1998	US 5686360 A EP 0777280 A JP 9161967 A	11-11-1997 04-06-1997 20-06-1997
WO 9212219 A	23-07-1992	AU 1243092 A BR 9205462 A CA 2096826 A EP 0566683 A JP 6504387 T US 5867238 A	17-08-1992 01-03-1994 12-07-1992 27-10-1993 19-05-1994 02-02-1999
EP 0977469 A	02-02-2000	NONE	

**This Page is Inserted by IFW Indexing and Scanning
Operations and is not part of the Official Record**

BEST AVAILABLE IMAGES

Defective images within this document are accurate representations of the original documents submitted by the applicant.

Defects in the images include but are not limited to the items checked:

- ☐ BLACK BORDERS
- ☐ IMAGE CUT OFF AT TOP, BOTTOM OR SIDES
- ☐ FADED TEXT OR DRAWING
- ☒ BLURRED OR ILLEGIBLE TEXT OR DRAWING
- ☐ SKEWED/SLANTED IMAGES
- ☐ COLOR OR BLACK AND WHITE PHOTOGRAPHS
- ☐ GRAY SCALE DOCUMENTS
- ☐ LINES OR MARKS ON ORIGINAL DOCUMENT
- ☐ REFERENCE(S) OR EXHIBIT(S) SUBMITTED ARE POOR QUALITY
- ☐ OTHER: _____

IMAGES ARE BEST AVAILABLE COPY.

As rescanning these documents will not correct the image problems checked, please do not report these problems to the IFW Image Problem Mailbox.